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FLUORINE GENERATOR SOLID INGREDIENT DEVELOPMENT  
FINAL REPORT

2

ROCKETDYNE DIVISION  
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## FOREWORD

This final report was prepared by the Rocketdyne Division, Rockwell International Corporation, 6633 Canoga Avenue, Canoga Park, California 91304 for the Air Force Rocket Propulsion Laboratory, Edwards, California 93523 and covers work from 1 July 1974 to 30 June 1975 conducted under Air Force Contract F04611-74-C-0035, Job Order No. 197000HM.

The project monitor was Capt. Ronald E. Channell. This program was conducted by the Exploratory Chemistry Unit of the Energy Systems and Technology Organization, Advanced Programs, with Dr. B. L. Tuffly serving as Program Manager and Dr. Ross I. Wagner as project engineer. Major contributors to the program were Dr. Carl J. Schack (UV process evaluation) and Mr. Richard D. Wilson (metathetical process evaluation and UV process scale-up and synthesis). Dr. Victor H. Dayan was responsible for analyses and Drs. Karl O. Christe, Arthur E. Axworthy, Louis R. Grant and Frederick D. Raniere contributed significantly as consultants.

This effort was sponsored by the Air Force Rocket Propulsion Laboratory, Edwards, CA., the Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico, and the Naval Surface Weapons Center, Silver Springs, Maryland.

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The UV process was scaled-up to achieve a production rate of 2.90 g/hr of 99 mole percent  $\text{NF}_4\text{BF}_4$  with an 84 percent conversion of reactants. Although process optimization was not achieved due to insufficient time, approximately 0.32 Kg  $\text{NF}_4\text{BF}_4$  was produced and delivered to the Air Force.

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## SUMMARY

### EVALUATION OF ALTERNATE SYNTHESIS TECHNIQUES - PHASE I, TASK 1

Two preparative methods for  $\text{NF}_4\text{BF}_4$  of substantially different concept were evaluated for achievable product purity and scalability. The two preparative methods evaluated were (1) the UV-induced reaction of  $\text{NF}_3$ ,  $\text{BF}_3$  and  $\text{F}_2$ , and (2) the metathetical conversion of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  to  $\text{NF}_4\text{BF}_4$ .

An evaluation of the UV-induced synthesis of  $\text{NF}_4\text{BF}_4$  established that high purity (minimum 99 mole percent) material could be prepared on a small scale in a silica reactor at a rate, ~1g/hr during short reaction times, potentially capable of providing the material at a practical production rate. The most important process parameters established during these studies were (1) cryogenic temperatures, (2) high UV intensity, (3) the mode of addition of reactants to maintain exposure to the radiation, and (4) the mole ratios of the reactants.

The metathetical process was evaluated and the maximum purity obtained for the  $\text{NF}_4\text{BF}_4$  was 93 mole percent. It was established that: (1) TlF was better than AgF as a precipitant for  $\text{SbF}_6^-$ ; (2)  $\text{NF}_4\text{BF}_4$  prepared using AgF rather than TlF was of higher purity because of the more complete removal of excess metal fluoride in the second step of the process (i.e., formation of  $\text{AgBF}_4$ ); (3)  $\text{Cl}^-$  ion could not be used to remove additional metal fluoride from the product because of incompatibility with  $\text{NF}_4^+$ ; and (4) the major impurity  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  was, in fact, less soluble than  $\text{NF}_4\text{BF}_4$  rendering purification by crystallization unfeasible.

On the basis of these experimental evaluations, the UV process was selected for scale-up.

### SYNTHESIS SCALE-UP - PHASE I, TASK 2

A large-scale UV reactor was designed and fabricated using 347 stainless steel and Teflon-gasketed sapphire windows as materials of construction. By use of those conditions established under Task 1, the production rate objective of 80g  $\text{NF}_4\text{BF}_4$ /week of 99 mole percent purity was achieved. This objective was

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fulfilled even though optimization of the process parameters was not realized.

#### LARGE-SCALE SYNTHESIS OF $\text{NF}_4\text{BF}_4$ - PHASE II

Investigation of the process parameters of the UV process was continued during production of a total of 0.37 kg of  $\text{NF}_4\text{BF}_4$ . Despite the successful preparation and delivery of 0.24 kg of 99 mole percent  $\text{NF}_4\text{BF}_4$  to the Air Force during this phase, only qualitative data correlating product formation rate with process variables were obtained. This inability to achieve quantitative data was primarily the result of reactor design deficiencies not readily correctable within the contractual time frame. However, evidence was obtained that, under certain conditions,  $\text{NF}_4\text{BF}_4$  was synthesized at 2.90g/hour with a conversion of 84 percent.

## INTRODUCTION

A solid-propellant fluorine generator would have obvious logistic advantages over conventional gas storage or cryogenic liquid supply systems for the fluorine required to operate a C.W. chemical laser based on a DF lasing species. Ideally, a practical solid-propellant fluorine generator requires a compatible oxidizer-fuel-binder combination that provides a completely gaseous exhaust containing only stable, non-reactive, and non-deactivating co-products. A potential system which meets these ideal requirements is that based on the oxidizer  $\text{NF}_4\text{BF}_4$  in combination with a fluorocarbon fuel binder.

The purpose of the work described herein was to develop a process for the synthesis of high purity (99 mole percent minimum)  $\text{NF}_4\text{BF}_4$  which would provide sufficient quantity of this oxidizer to permit its evaluation as an ingredient in a solid-propellant fluorine generator. Specific objectives were: (1) to evaluate two synthetic processes for  $\text{NF}_4\text{BF}_4$  of substantially different concept; (2) to select on the basis of product purity and potential scalability one process and experimentally demonstrate its scalability to the production level of at least 80g/week; and (3) to produce and deliver to the Air Force 0.24 Kg of high purity  $\text{NF}_4\text{BF}_4$ .

Of the four processes for preparation of  $\text{NF}_4\text{BF}_4$  known at the inception of this work, the two selected for evaluation were: (1) the UV-induced combination of  $\text{NF}_3$ ,  $\text{BF}_3$ , and  $\text{F}_2$  (Ref. 1) and (2) the metathesis of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  (Ref. 2) with  $\text{AgHF}_2$  (Ref. 3) and treatment of the resulting  $\text{NF}_4\text{HF}_2$  with  $\text{BF}_3$ . The UV process was selected on the basis of its high potential for producing directly a high purity product and the assumption that the production rate could be raised from the previously observed milligram quantities to a practical level. The metathetical process was chosen because it represented the most advanced (Ref. 3) preparative method in terms of production rate, and conventional purification techniques might raise the purity to the required level. Of the remaining two processes,  $\gamma$ -irradiation (Ref. 4) and glow discharge (Ref. 5 and 6) both were rejected because of the projected difficulty of scale-up.

## DISCUSSION OF RESULTS

### UV PROCESS - PHASE I, TASK 1

At the inception of this contract, only one reference to a UV-induced synthesis of  $\text{NF}_4\text{BF}_4$  was known (Ref. 1). This reaction, which involved UV irradiation of an equimolar mixture of  $\text{NF}_3$ ,  $\text{F}_2$  and  $\text{BF}_3$ , offered a potential means for acquiring pure  $\text{NF}_4\text{BF}_4$  by a single step process. However, in the single reported experiment on which this synthesis was based, only 1 to 2 mg of product was obtained when the reaction was conducted in a sapphire tube reactor at ~90 psig and ambient temperature. Although this amount of  $\text{NF}_4\text{BF}_4$  was produced rapidly, further increase in the amount of product did not occur on continued exposure to the UV source. The exceedingly low conversion of the gaseous reactants to  $\text{NF}_4\text{BF}_4$  was attributed to deposition of solid product on the sapphire reactor walls. This deposit if opaque to UV light might preclude sufficient transmission of light energy required for further reaction.

The major scaleup problem associated with the UV-induced synthesis of  $\text{NF}_4\text{BF}_4$  appeared to be development of a method by which a UV-transparent window could be kept free of product. Several possible solutions to this problem were considered, and the one that appeared to be the simplest was the use of HF as a solvent for the  $\text{NF}_4\text{BF}_4$ . Since HF is both UV-transparent (Ref. 7) and an excellent solvent for  $\text{NF}_4\text{BF}_4$  (Ref. 2), it was proposed that its presence in the gaseous reaction mixture would cause the solid coating to deliquesce, drain off, and thereby maintain window UV transparency. With this approach in mind, the first of several reactors was designed, fabricated and used in the small scale UV-induced reactions for the purpose of evaluating this method for the production of pure  $\text{NF}_4\text{BF}_4$ .

#### UV Reactor Design (Small Scale)

The initial UV reactor consisted of a 8.5-inch Teflon test tube of 195 ml volume to which was attached a 2-inch diameter sapphire window with appropriate attachments for evacuation and gas filling. Before any experiments were conducted in the presence of HF, the experimental conditions required to synthesize

$\text{NF}_4\text{BF}_4$  in the new reactor had to be defined. Although conditions were found which produced  $\text{NF}_4\text{BF}_4$  in this Teflon-sapphire reactor, none of the product was ever found to coat the window. A reactor of similar design in which stainless steel was used in lieu of Teflon was found to give similar results. These results differed from those previously reported by Christe et al. (Ref. 1). Although reactions were investigated under conditions of high pressures and ambient temperature (see Appendix I), such reactions produced no  $\text{NF}_4\text{BF}_4$ . Under the conditions whereby  $\text{NF}_4\text{BF}_4$  was produced temperatures were lower than ambient and the product was formed away from the window. Hence, experiments using HF were unnecessary and were never attempted.

As the program progressed, it became obvious that the geometry of the reactor was far from optimum, and materials other than Teflon or Kel-F would be needed for construction of the reactor. Under the influence of the UV-derived fluorine atoms, Teflon was severely degraded as evidenced by shrinkage, embrittlement, stress cracking and formation of  $\text{CF}_4$ . Kel-F appeared to undergo an even more rapid degradation of physical properties with concomitant formation of per-fluoroalkyl chlorides.

Since the use of HF was not required to maintain the sapphire window transparency, fused silica was used to construct the second type of reactor. This reactor was a 3-inch diameter bulb fitted with an O-ring joint and Fischer-Porter needle valve for evacuation and introduction of the gaseous reactants. Although surface attack of the silica did occur (Eq. 1), weight loss of the



reactor (with a 100 watt UV source) was only about 1 mg/hr and no byproducts were found to contaminate the  $\text{NF}_4\text{BF}_4$ . The lightweight silica bulb allowed gravimetric determination of the extent of reaction to be made conveniently in place of the manometric method which was used with the much heavier Teflon- or stainless-steel sapphire reactors. In addition to the more accurate method of measuring the  $\text{NF}_4\text{BF}_4$  formation rate, the diameter of the silica bulb allowed the UV source to be placed closer to the temperature-controlled reaction zone. This led to a significant improvement in the formation rate of  $\text{NF}_4\text{BF}_4$ .

The third reactor design provided a further improvement in geometry by incorporating a 3-inch diameter, flat window in the shallow (1-1/4 inch) silica reactor. This permitted the light source to be even closer to the reaction zone, and reflection losses were decreased as well. Both of these factors contributed to additional increases in the  $\text{NF}_4\text{BF}_4$  formation rates.

#### Reaction Parameters

A number of variables, not necessarily independent, were considered for study to determine their effect on the rate of formation of  $\text{NF}_4\text{BF}_4$ . They were (1) temperature, (2) UV light intensity, (3) mode of addition of reactants, (4) reactant mole ratios, (5) pressure, (6) catalysts, and (7) use of HF to dissolve  $\text{NF}_4\text{BF}_4$  coated on the reactor window. Of these only the last was not investigated, since  $\text{NF}_4\text{BF}_4$  was not found to coat the window as reported in the original UV-initiated synthesis. Selected experiments which illustrate the effect of a given parameter on the  $\text{NF}_4\text{BF}_4$  formation rate are presented in the tables accompanying the discussion of that parameter. Complete data for each of the eighty-four experiments conducted during the evaluation phase of the UV-induced synthesis of  $\text{NF}_4\text{BF}_4$  are tabulated in Appendix I.

Effect of Temperature. Because of the obvious economic advantages of an ambient temperature process over one requiring refrigeration, a number of unsuccessful attempts were made to synthesize  $\text{NF}_4\text{BF}_4$  at ambient temperature by the UV-initiated method. Typical experiments which indicate the effect of temperature on the rate of formation of  $\text{NF}_4\text{BF}_4$  are listed in Table 1. Unless otherwise noted, comparable conditions were used in the tabulated experiments.

It is apparent from experiments 1, 5 and 12 (which used the same reactor) that as temperature is decreased the formation rate of  $\text{NF}_4\text{BF}_4$  is increased. This effect is most pronounced at cryogenic temperatures and has been rationalized as the result of stabilization of a reaction intermediate. The dramatic rate increase shown in experiments 36 and 55, when compared with 13 and 14, clearly emphasized the need for cryogenic temperatures, if a high production rate of  $\text{NF}_4\text{BF}_4$  were to be achieved. The somewhat larger and seemingly anomalous rate observed at -115 C compared with that at -140 C is in reality the effect of intermittent addition of larger amounts of  $\text{BF}_3$  (vide infra).

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TABLE 1. EFFECT OF TEMPERATURE ON  $\text{NF}_4\text{BF}_4$  FORMATION RATE

Experiment No.	Reaction Temp., $^{\circ}\text{C}$	Photolysis Time, hrs.	Mole Ratio $\text{BF}_3/\text{NF}_3$	$\text{F}_2/\text{NF}_3$	Pressure Range (during photolysis), mm	Reactor Used(a)	$\text{NF}_4\text{BF}_4$ Formation Rate, mg/hr
1	amb.	18	1	1	-650	TS	0
5	-78	10	1	2	700-690	TS	Trace
13 (b)	-115	2	3.3	0.9	800-500	SB	3.5
14 (b)	ca. -140	2	1.1	0.25	500-350	SB	1.7
12	-186	8	1	2	-250	TS	8
55	-186	2	1	0.83	370-350	SB	34.5
36	-196	2	1	0.5	220-165	SB	33

(a) TS = Teflon-sapphire; SB = silica bulb

(b) Reactants introduced intermittently during photolysis rather than before photolysis as in other experiments  
(Refer to Appendix I for details).

Effect of UV Intensity. A series of experiments (64 and 39-42, Table 2) was conducted in which the intensity of the UV source was diminished by insertion of stainless steel screens between the light source and the photolysis zone. The percent transmittance of the screens was measured spectrometrically at both 578  $\mu\text{m}$  and 400  $\mu\text{m}$ . The average of the two values (approximately 1 percent difference) was used as the percent transmittance of the screens. The  $\text{NF}_4\text{BF}_4$  formation rate was not found to be proportional to intensity (percent transmittance) raised to a constant power. The values for  $n$  in the equation  $R = kI^n$  (where  $R$  is rate and  $I$  is intensity) were 0.426, 0.561, and 0.720 for screens with 49.5, 36.3, and 33.0 percent transmittance, respectively.

The apparent curvature of the plot of  $\log R$  vs  $\log I$  may be only an artifact arising from geometric factors. The three screens used had the following characteristics: 49.5% transmittance ( $T$ ), 64 mesh, wire diameter ( $w$ )/hole width ( $h$ ) = 0.224; 33.0%  $T$ , 35 mesh,  $w/h = 0.735$ ; and 36.3%  $T$ , 150 mesh,  $w/h = 0.556$ . The percent transmittance of the screens was measured virtually normal to the plane of the screen by the nearly parallel light beam in the spectrophotometer. In contrast, the UV light irradiating the reaction zone in the photolysis experiments approximated a divergent cone with an apical angle of  $60^\circ$ . The amount of light passing a screen will decrease as the angle of incidence decreases, and for a given angle of incidence will decrease most with thick screens, i.e., when  $w/h$  is largest. The observed correlation of the rates of formation of  $\text{NF}_4\text{BF}_4$  with light intensity (assuming normal incidence) is as expected for the geometries involved. From these considerations, the rate of  $\text{NF}_4\text{BF}_4$  formation would be expected to increase by a factor somewhat greater than the maximum observed, i.e.,  $R > kI^{0.426}$ .

With all factors other than UV lamp wattage held reasonably constant, the  $\text{NF}_4\text{BF}_4$  formation rate was almost directly proportional to the power input (Table 2, experiments 67, 69 and 75). The decrease in  $\text{NF}_4\text{BF}_4$  formation rate with distance between lamp and photolysis zone (Table 2, experiments 61 and 67) more closely approximates that expected from a point source ( $\propto 1/d^2$ ) than from a linear source ( $\propto 1/d$ ).

TABLE 2. EFFECT OF UV INTENSITY ON  $\text{NF}_4\text{BF}_4$  FORMATION RATE (a)

Experiment No.	Pressure Range (during photolysis), mm	Reactant Used (b)	Lamp to Condensed Reactant Distance, cm	Percent Transmission	$\text{NF}_4\text{BF}_4$ Formation Rate, mg/hr
64	130-70	SB	12	100	30
39	85-50	SB	12	49.5	21.5
40	80-45	SB	12	49.5	23
41	80-55	SB	12	36.3	17
42	80-50	SB	12	33.0	13.5
61	115-70	SF	9(c)	100	71
67	210-100	SF	7.5(c)	100	110
69	~200	SF	7.5(c)	100	1004
75	~175	SF	7.5(c)	100	1172

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(a) All experiments were conducted at -196°C for 2 hours in the same reactor using a  $\text{NF}_3/\text{BF}_3/\text{F}_2$  reactant mole ratio of 1/1/0.17, respectively.

(b) SB = silica bulb; SF = silica flat-windowed reactor (see Appendix I).

(c) Experiments 67 and 61, 100 watt Hanovia (lamp B); experiments 69, 1000 watt G.E., lamp BH6; experiment 75, 1000 watt III lamp BH6-1-B; other experiments, 100w Hanovia (lamp A).

Mode of Addition of Reactants. Three modes of reactant addition were evaluated: (1) addition of all reactants before initiation of photolysis, (2) continuous introduction of reactants during photolysis, and (3) intermittent addition of reactants during photolysis. The photolysis is best conducted at cryogenic temperatures and under these conditions the  $\text{BF}_3$  and  $\text{NF}_3$  are found almost entirely in the condensed phase, while  $\text{F}_2$  is distributed between the condensed and gaseous phases. The rate at which the reactants are introduced, as well as the order of introduction (if not premixed), affects the physical state of the condensed phase. While not all of the parameters were held constant in the experiments listed in Table 3, the range over which these vary is not sufficient to invalidate comparison of  $\text{NF}_4\text{BF}_4$  formation rates.

The rate of  $\text{NF}_4\text{BF}_4$  formation is greater when condensation is effected rapidly (2-3 minutes in mode B, Table 3) as can be seen by comparing Experiments 32 and 27. In the latter experiment condensation occurred over a 60 minute period prior to photolysis and the rate of  $\text{NF}_4\text{BF}_4$  formation was decreased from 27 to 14 mg/hr. However, if the slow condensation is carried out continuously during photolysis (Experiment 29), the rate is increased to 19 mg/hr indicating the beneficial effect of the continuous mode of addition.

Intermittent addition of reagents should combine the best features of both the pre-photolysis and continuous modes in that rapid condensation of each increment would occur and fresh reagents would be added during the photolysis period. Comparison of Experiments 58 (addition before photolysis) and 11 (intermittent addition during photolysis) does not appear to support the hypothesis that intermittent addition is the best mode. However, other experiments conducted at a higher UV intensity (vide infra) do verify the hypothesis, and the apparent anomaly observed here presumably arises because the sequence of reactions leading to  $\text{NF}_4\text{BF}_4$  is inhibited by swamping with fresh reagents. In the series of experiments of varying photolysis time wherein all reagents were added before photolysis (Experiments 69, 71, 72 and 74), the  $\text{NF}_4\text{BF}_4$  formation rate decreased drastically with time. The average hourly rate during the last two hours of the three hour photolysis decreased from an initial 1 g/hr rate (during the first 0.25 hr) to less than 20 percent of this value. Intermittent addition of reagents under comparable conditions (Experiment 84) maintained the average  $\text{NF}_4\text{BF}_4$  formation rate in a 4 hour photolysis at nearly

TABLE 3. EFFECT OF MODE OF ADDITION OF REAGENTS ON  $\text{NF}_4\text{BF}_4$  FORMATION RATE (a)

Experiment No.	Photolysis Time, hrs	Mole Ratio $\text{BF}_3 / \text{NF}_3$	Mode of Reactant Addition (b)	Pressure Range (during photolysis), mm	Reactor Used	UV Lamp Type	Average $\text{NF}_4\text{BF}_4$ Formation Rate, mg/hr
32	2	4.67	0.56	200-120	SB	H(A)	27
27	1	4.67	0.56	350-185	SB	H(A)	14
29	1	4.67	0.56	350-190	SB	H(A)	19
58	2	1	0.30	180-120	SB	H(A)	37.5
11	3	1	0.29	150 ± 20	SB	H(A)	20
69	0.25	1	0.17	~200	SF	GE	1004
71	0.5	1	0.33	~225	SF	GE	888
72	1	1	0.33	200-175	SF	GE	804
74	3	1	0.43	500-225	SF	GE	391
84	4	1	0.21	1	SF (d)	GE	647

(a) All experiments were run at -196 °C.

(b) B, before photolysis; C, continuous during photolysis; and I, intermittent addition.

(c) All reactants were introduced exactly as in Experiment 29 but before photolysis.

(d) Reactor inlet in center of photolysis zone.

double the value of the 3 hour photolysis where reagent addition preceded photolysis. A conversion of 83 percent was observed in Experiment 84 based on the limiting reactant ( $F_2$ ).

These data suggested that maximization of the  $NF_4BF_4$  formation rate over extended times (as would be required in a production process) would best be accomplished by intermittent addition of reagents to the photolysis zone. Sufficient time should be allowed between additions to permit optimum utilization of the reagents in each increment.

Effect of Reactant Mole Ratios. Equimolar amounts of  $NF_3$ ,  $BF_3$  and  $F_2$  are required to prepare  $NF_4BF_4$  by the UV-initiated synthesis. However, since the reaction mechanism is unknown, the rate-determining step might be favored by a deviation from the stoichiometric ratio.

From a practical experimental standpoint, sequential condensation of the three gaseous reagents into a reactor at -196 C should proceed from the least volatile to the most volatile, i.e.,  $BF_3$ ,  $NF_3$  and, finally,  $F_2$ . Condensation of  $BF_3$  alone, or even when premixed with  $NF_3$ , tends to form a rather compact solid mass due to prior liquefaction. However, if the condensation occurs in a fluorine atmosphere, the condensation rate is slowed somewhat so that a porous solid structure results. The structure of the condensed phase appears to affect the  $NF_4BF_4$  formation rate, perhaps, as a result of varying ease of mass transport of the liquid  $BF_3$ - $NF_3$ - $F_2$  solution through the porous solid  $BF_3$ .

In Table 4 the relative effects of an excess of one of the three starting materials on the rate of formation of  $NF_4BF_4$  is illustrated. The most detrimental ingredient when in excess was  $NF_3$ , which inhibited  $NF_4BF_4$  formation completely. Less drastic in its effect was excess  $F_2$ , but much of this reagent is in the gaseous phase. An excess of  $BF_3$  appears either to be without effect or possibly may even increase the rate of  $NF_4BF_4$  formation based on extrapolation from experiments in a different reactor. No directly comparable experiment in the same reactor using a stoichiometric ratio was conducted.

Effect of Pressure. In all of the experiments which were designed to test the effect of pressure on the  $NF_4BF_4$  formation rate, the temperature of necessity had to be above cryogenic levels where  $NF_4BF_4$  formation is extremely inhibited.

TABLE 4. EFFECT OF REAGENT MOLE RATIOS ON  $\text{NF}_4\text{BF}_4$  FORMATION RATE (a)

Experiment No.	Pyrolysis Time, hrs	Mole Ratio $\frac{\text{BF}_3}{\text{NF}_3}$	Mole Ratio $\frac{\text{F}_2}{\text{NF}_3}$	Mode of Reactant Addition	Pressure Range (during photolysis), mm	Average $\text{NF}_4\text{BF}_4$ Formation Rate, mg/hr
23	1	1	7.8	C	~350	14
22	2	1	4.4	C	~350	29.5
20	2.5	0.21	0.21	I (b)	200-100	0
21	1.75	4.67	0.67	C	300-250	47

(a) All experiments were conducted at -196°C in a 3-inch stainless steel reactor with a 2-inch diameter sapphire window and the same 100 watt UV source.

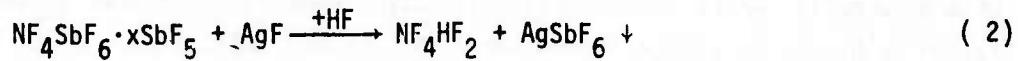
(b) One-third of the total  $\text{F}_2$  used was added after 1 hour photolysis.

Since low temperatures have proved to be perhaps the most important requirement for successful  $\text{NF}_4\text{BF}_4$  synthesis, the pressure range which could be studied is quite limited. Pressure becomes a dependent variable determined by both the temperature and the reactant mole ratio. From the available data, no effect on  $\text{NF}_4\text{BF}_4$  formation rate can be ascribed to pressure alone.

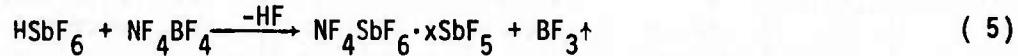
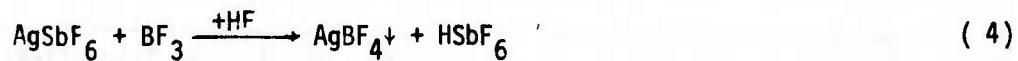
Effect of Catalysts. In some of the first experiments where Kel-F components were used in the reactors, the formation of small amounts of  $\text{ClF}_5$  was observed. In some of these experiments  $\text{NF}_4\text{BF}_4$  was also formed and the possibility that  $\text{ClF}_5$  was catalyzing the formation of  $\text{NF}_4\text{BF}_4$  was considered. Addition of  $\text{ClF}_5$  to the reaction mixtures was subsequently observed to be ineffective and was discontinued.

## METATHETICAL PROCESS - PHASE I, TASK 1

Prior to this contractual effort,  $\text{NF}_4\text{BF}_4$  had been produced at Rocketdyne in a purity of  $86 \pm 3$  mole percent and 70 percent yield in runs on a 0.8 mole scale. The metathesis was accomplished by the reactions shown in Eq. 2 through 5. The



major contaminants in the  $\text{NF}_4\text{BF}_4$  product were found to be  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  and  $\text{AgBF}_4$ , and the presence of these impurities was attributed to the following reactions:



For the purpose of improving both the yield and purity of the metathetically-derived  $\text{NF}_4\text{BF}_4$ , several process improvements were investigated. These were: (1) attempts to insure the use of water-free HF (the salt is known to hydrolyze readily); (2) preparation of  $\text{NF}_4\text{SbF}_6$  containing a smaller amount of complexed  $\text{SbF}_5^-$ ; and (3) the use of  $\text{SbF}_6^-$  precipitants other than  $\text{AgF}$ . In addition to these studies, estimates of the solubility of  $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$  and T1F in HF were obtained, as well as the densities of such solutions. These data were required to maximize the batch quantities of  $\text{NF}_4\text{BF}_4$  prepared in the volume-limited reactor. Finally, investigations were conducted to upgrade the crude  $\text{NF}_4\text{BF}_4$  by reprocessing, chemical reaction and recrystallization.

### Attempted Analysis for Water in HF Solutions

Since  $\text{NF}_4\text{BF}_4$  is hydrolytically unstable, minimizing the water content of the reagents used in the metathetical synthesis would be expected to give an increased yield of higher purity product. Accordingly, an attempt was made to develop a quantitative analytical method for water in the solvent HF applicable also to reagent solutions in HF. The proposed method was based on the hydrolysis of the thermally produced (and, hence, water-free) salt  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ . It was expected that  $\text{NF}_3$  generated by reaction of a few milligrams of  $\text{H}_2\text{O}$  with this antimony salt could be determined quantitatively using the very strong  $\text{NF}_3$  infrared absorbance at  $907 \text{ cm}^{-1}$ .

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The amount of  $\text{NF}_3$  formed on reaction of a known quantity of water in HF with an excess of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  was but a few percent of theoretical (see Table 5). To explain these low results, it is postulated that the complex salt in HF behaves as a solution of  $\text{NF}_4\text{SbF}_6$  and  $\text{HSbF}_6$ , and in the resulting extremely acidic solution the water is protonated almost completely. As a consequence, a reaction between the cations,  $\text{NF}_4^+$  and  $\text{OH}_3^+$ , would not be very probable. In line with this hypothesis, water (completely protonated) when introduced as  $\text{OH}_3\text{SbF}_6$  (Ref. 8) failed to hydrolyze a significant amount of the  $\text{NF}_4^+$  salt (Table 5). In view of these results, no additional work was performed for the analysis of water in HF or its solutions.

TABLE 5. ANALYSIS OF WATER IN HF<sup>(a)</sup>

Sample No.	Wt. of HF, g	Wt. of $\text{H}_2\text{O}$ , mg	Vol. of $\text{NF}_3$ , cc	% of Theoretical $\text{NF}_3$ Recovered
1	2.3226	2.30	0.129	4.5
2	1.0155	1.00	0.034	2.7
3	1.4591	1.45	0.099	5.5
4	2.3605	2.38	0.020	0.68
5	9.7	10.74 <sup>(b)</sup>	0.191	1.7

(a) HF- $\text{H}_2\text{O}$  solution added to known quantities of  $\text{NF}_4\text{SbF}_6 \cdot 0.8 \text{SbF}_5$

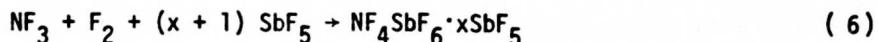
(b) Weighed directly as 0.1520g  $\text{OH}_3\text{SbF}_6$

Solubility and Density Studies. In order to maximize the amount of  $\text{NF}_4\text{BF}_4$  per batch in the metathetical synthesis from  $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$ , the solubility of this starting material and the density of its HF solution were required. The data obtained must be considered as approximate only since the composition of the salt varies slightly with each batch (vide infra, Table 6). The solubility of  $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$  was found to be 5.1 g/g HF at 0.5 C and 8.5 g/g HF at 28.5 C by visual observation of dissolution of weigh quantities of solute and solvent. The density of the latter solution was determined to be 2.4 g/ml.

Data from a similar study of  $\text{TlF}$  solutions were invalid because the solution was fluorine-dried and only part of the  $\text{TlF}_3$  formed precipitated, while the rest remained in solution as complex anionic species.

### $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ Preparative Studies

The antimony salt,  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ , is the most readily prepared source of  $\text{NF}_4^+$  cation and, as such, was used as the starting material in the metathetical synthesis of  $\text{NF}_4\text{BF}_4$ . Of the several known methods for its preparation, the thermal activation process is the best for preparing relatively large amounts in a minimum time (Eq. 6). The product obtained is a solid with variable



composition (i.e.,  $x = 3$  to  $4$ ). The amount of  $\text{SbF}_5$  complexed by the  $\text{NF}_4\text{SbF}_6$ , when the salt is used as an intermediate for the synthesis of  $\text{NF}_4\text{BF}_4$ , should be as small as possible since the excess  $\text{SbF}_5$  increases the amount of metal fluoride required for the precipitation of  $\text{MSbF}_6$  (Eq. 2).

Prior to the  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  preparative studies conducted under this contract, a number of large-scale runs had been made at  $115^\circ\text{C}$  (Runs 1-6, Table 10, see Experimental Section). The ratio of Sb/N in the product salt was in the range 3-4 and required vacuum pyrolysis at  $200^\circ\text{C}$  for 24 hours or longer to distill off the excess  $\text{SbF}_5$ . The Sb/N ratio of the final product was approximately 1.8-2.0.

In view of the fact that partial depolymerization of the complex anion could be accomplished at  $200^\circ\text{C}$ , attempts were made to produce  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  with a lower Sb/N ratio directly from the gaseous reactants, without post pyrolysis. This approach was based on the assumption that, at the  $115^\circ\text{C}$  reaction temperature, the product with a Sb/N ratio of 3 to 4 may have been stabilized due to crystallization from the fluid mixture. If this assumption were correct, then higher reaction temperatures might yield higher melting salts of lower antimony content.

Several syntheses were conducted at temperatures higher than  $115^\circ\text{C}$ . At both  $200$  and  $250^\circ\text{C}$ , the Sb/N ratio of the products remained in the range 3 to 4, and the post preparative pyrolysis step was required to remove excess  $\text{SbF}_5$ . A slightly greater attack of the Monel reactor at these temperatures was noted by the increased quantity of nickel and copper salts accompanying the

$\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ . An appreciable amount of these relatively insoluble nickel and copper salts were removed by filtration during extraction of the product from the Monel reactor with HF. Analytical data and calculated composition of the products for the high temperature runs are summarized in Table 6.

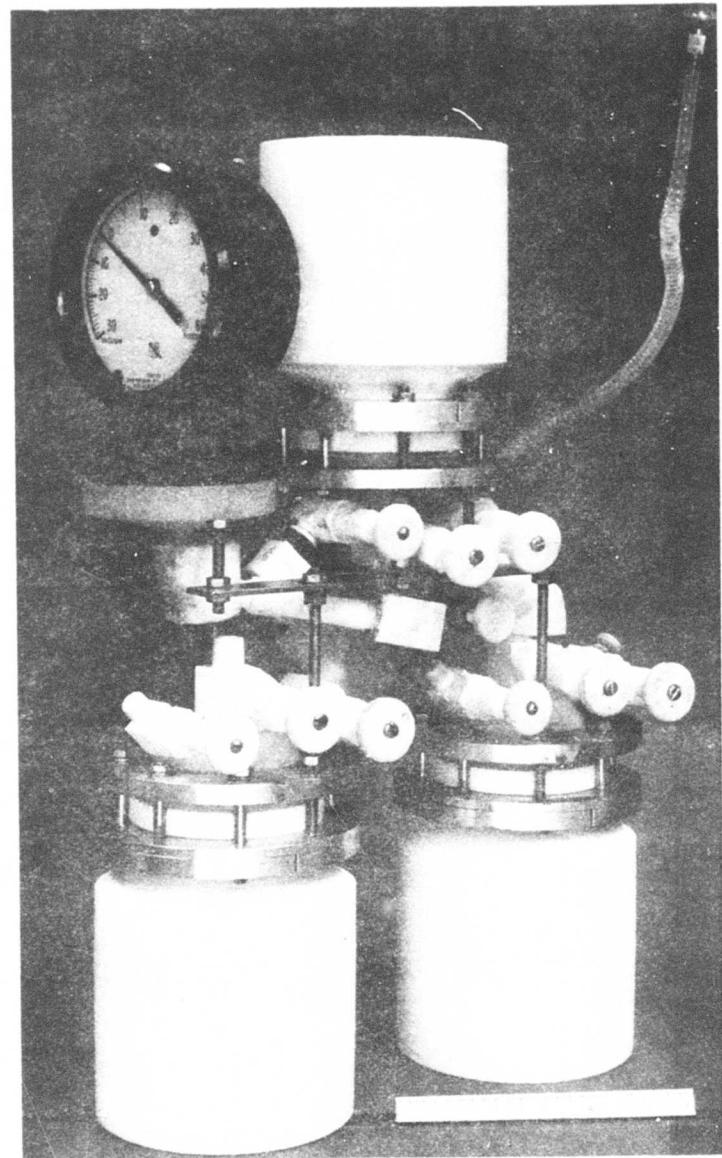
Since the higher temperatures were not useful for a direct synthesis of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  with a low Sb/N ratio, all other preparative runs were made at 115°C to provide the starting material for the metathetical synthesis of  $\text{NF}_4\text{BF}_4$ .

#### $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ Metathesis to $\text{NF}_4\text{BF}_4$

To achieve the specified 99-mole percent pure  $\text{NF}_4\text{BF}_4$  by the metathetical route, the first approach was to substitute thallous fluoride for AgF as the  $\text{SbF}_5^-$  precipitant (Eq. 2). Although  $\text{NF}_4\text{BF}_4$  had been previously synthesized at Rocketdyne and elsewhere by the metathetical route, the maximum purity of the salt (without post treatment) never exceeded 86 ± 3 mole percent. It was believed that an increase in the purity of  $\text{NF}_4\text{BF}_4$  could be realized if the  $\text{Ag}^+$  ion were replaced in the metathesis by another cation which formed less soluble  $\text{SbF}_6^-$  and  $\text{BF}_4^-$  salts. This conclusion was reached on the basis of the knowledge that both  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  and  $\text{AgBF}_4$  are present as contaminants in the  $\text{NF}_4\text{BF}_4$ , and their presence is most likely due to reactions such as represented by Eq. 4 and 5.

Metathesis Using TlF. Of the metals forming HF-soluble fluorides, only thallium appeared to be a better precipitant candidate for  $\text{SbF}_6^-$  than silver. The reported solubility data for  $\text{TlSbF}_6$  in HF (Ref. 9) indicated a solubility almost an order of magnitude less than that of  $\text{AgSbF}_6$  (0.019M vs. 0.16M; the latter was estimated from antimony analyses of  $\text{NF}_4\text{BF}_4$ ). No information, however, had been previously reported either on the solubility of  $\text{TlBF}_4$  in HF or on the compatibility of  $\text{NF}_4^+$  and  $\text{Tl}^+$ .

A preliminary experiment on a 10 mmole scale demonstrated that little  $\text{Tl}^+$  was oxidized to  $\text{Tl}^{+3}$  by  $\text{NF}_4^+$ . The evidence for this was that only a small amount of  $\text{NF}_3$  was formed during the reaction. Since there appeared to be no  $\text{Tl}^+ - \text{NF}_4^+$  compatibility problem, a 0.2 mole metathesis experiment was conducted in the large-scale reactor (Fig. 1) using TlF in place of AgF. The  $\text{NF}_4\text{BF}_4$  isolated from this experiment had an antimony content approximately four times less than that using AgF.



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Figure 1. Metathesis Apparatus

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TABLE 6 . ANALYSIS AND COMPOSITION OF HF SOLUBLE  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  PREPARATIONS

Run No.	Sample wt., mg	$\text{NF}_3$ , umoles	Sb, μg-at	Ni, μg-at	Cu, μg-at	Sb/N	Calculated Composition $\text{M}(\text{SbF}_6)_n \cdot x\text{SbF}_5$ , Mole Percent		
							$\text{M} = \text{NF}_4^+$	$\text{M} = \text{Ni}^{+2}$	$\text{M} = \text{Cu}^{+2}$
7	9.2	18.0	33.4	0.30	0.24	1.86	0.75	97.1	1.6
8 (a)	6.4	0.54	27.7	6.39	3.54	51.3	0.36	5.2	33.8
9	10.1	18.0	34.2	1.87	0.31	1.90	0.53	89.2	9.3
10	12.0	22.0	44.8	1.11	0.24	2.04	0.82	94.2	4.8

(a) During the post preparative pyrolysis step, the temperature control failed resulting in a temperature excursion and extensive decomposition of the  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ .

However, the purity of the  $\text{NF}_4\text{BF}_4$  was found to be lower than that produced by the use of  $\text{AgF}$ . This lower purity resulted from the presence of appreciable quantities of thallium in the product. The exact form in which the thallium was present is unknown; however, the most likely forms are  $\text{TlBF}_4$  and/or perhaps soluble  $\text{Tl}^{+3}$  complexes. The high toxicity of thallium coupled with the fact that attempts to decrease the thallium content of the  $\text{NF}_4\text{BF}_4$  were unsuccessful (vide infra) eliminated this reagent from further consideration.

Metathesis Using  $\text{AgF}$ . The scale of the metathetical reaction between  $\text{AgF}$  and  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  was increased from the normal 0.8 mole runs to 1.5 to 2.0 moles of the  $\text{NF}_4^+$  salt for the purpose of producing more of the product per batch. Problems associated with the removal of the coproduct  $\text{AgSbF}_6$  were encountered during these larger scale runs. The precipitation of the larger quantity of  $\text{AgSbF}_6$  resulted in a heat release that could not be rapidly dissipated by the Teflon equipment. This resulted in a product which contained a large amount of  $\text{AgSbF}_6$  due to the increased solubility of this coproduct under the experimental conditions used. Sufficient cooling of the  $\text{AgSbF}_6\text{-NF}_4\text{HF}_2$  slurry during the filtration step caused the  $\text{AgSbF}_6$  to precipitate in the filter and plug it.

Because of the marginal thermal stability of  $\text{NF}_4\text{HF}_2$  formed along with the  $\text{AgSbF}_6$ , long periods between mixing the  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  and  $\text{AgF}$  prior to filtration of the  $\text{AgSbF}_6$  could not be tolerated. Therefore, the HF solution of  $\text{AgF}$  was pre-cooled in an ice bath for about 0.5 hour prior to adding it to the HF solution of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ , followed by an additional 0.5 hour cooling period before carrying out the filtration step. This procedure worked well when 1.0 mole scale preparations were conducted, and would probably be adaptable to larger scale runs as well.

A second observation that was made during the larger scale runs was that the reaction of the filtrate, from the  $\text{AgF} - \text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  reaction, with  $\text{BF}_3$  required more agitation than was needed in the smaller runs. The required agitation was provided by manually shaking the reactor.

The synthesis and analytical data obtained for three metathetical runs are summarized in Table 7.

TABLE 7 . METATHETICAL  $\text{NF}_4\text{BF}_4$  PREPARATIONS

Run No.	Reactants, moles			Crude $\text{NF}_4\text{BF}_4$ , g	NF4BF <sub>4</sub> Purity, mole percent	Percent Yield	Analysis (mg Found)				
	NF <sub>4</sub> SbF <sub>6</sub> · xSbF <sub>5</sub>	AgF	BF <sub>3</sub>				Sample	NF <sub>3</sub>	B	Sb	Ag
9	0.95 (x = 0.89)	2.14	0.82	123.8	63 (a)	39	382.2	121.6	14.1	64.2	21.4
10	1.08 (x = 0.99)	2.22	1.40	164.2	90 (b)	65	372.1	117.4	18.4	37.8	11.9
11	0.94 (x = 0.91)	2.20	1.40	185.0	83 (b)	89	368.9	118.5	19.1	33.2	7.95

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22(a) Low purity attributed to contamination by AgSbF<sub>6</sub> because of non-cooling of the AgF-NF<sub>4</sub>SbF<sub>6</sub> · 0.95 SbF<sub>5</sub> reaction mixture.(b) HF solution of antimony salt was added to the HF solution of AgF precooled in an ice bath. The reaction mixture was retained in the ice bath for 40 minutes prior to filtration and reaction with BF<sub>3</sub>.

### Purification of Metathetical $NF_4BF_4$

Because the purity of the  $NF_4BF_4$  obtained directly from the metathetical reaction could not be increased by any of the approaches attempted, efforts were made to increase the purity of the material by other means. A crystallizer (Fig. 2) was built and used for recrystallizing the  $NF_4BF_4$  from HF. The procedure used for operating the crystallizer is described in the Experimental Section. Attempts were also made to upgrade the purity of the material by reprocessing the  $NF_4BF_4$ , and by reaction with HCl in HF. The results of these studies are presented below.

Crystallization Studies. Based on the assumption (since no density data or reliable solubility data were available) that  $NF_4BF_4$  is less soluble than  $NF_4SbF_6 \cdot xSbF_5$  in HF, it was believed possible to recover pure  $NF_4BF_4$  by crystallization from an HF solution of the mixed salts. The inseparable mixture that would be obtained after crystallization could then be metathetically reprocessed to enrich it in  $NF_4BF_4$ .

Experimentally,  $NF_4SbF_6 \cdot xSbF_5$  proved to be less soluble than  $NF_4BF_4$ , and, hence, it concentrated in the solid phase during crystallization. When a composite (470 g, calculated to consist of 84  $NF_4BF_4$ , 9.3  $NF_4SbF_6 \cdot 1.1 SbF_5$ , and 6.6 mole percent  $AgBF_4$ ) was taken of the metathetical runs shown in Table 7 and crystallized from HF, the results summarized in Table 8 were obtained. The filter cake

TABLE 8. CALCULATED COMPOSITIONS\* OF ISOLATED FRACTIONS  
FROM  $NF_4BF_4$  CRYSTALLIZATION

Sample	Weight, g	$NF_4BF_4$	$NF_4SbF_6 \cdot xSbF_5(x)$	$AgBF_4$	$AgSbF_6$
Composite of Runs 9-11	470	84.1	9.3 (1.1)	6.6	0
Insolubles Runs 9-11	23	5.0	3.6 (1.1)	91.4	0
Crystallized Filter Cake					
Center	180	74.0	23.4 (0.90)	0	3.0
Periphery		75.4	20.1 (0.90)	0	4.6
Filtrate Residue	250	93.0	5.9 (0.90)	0	1.1

\*Compositions given as mole percent

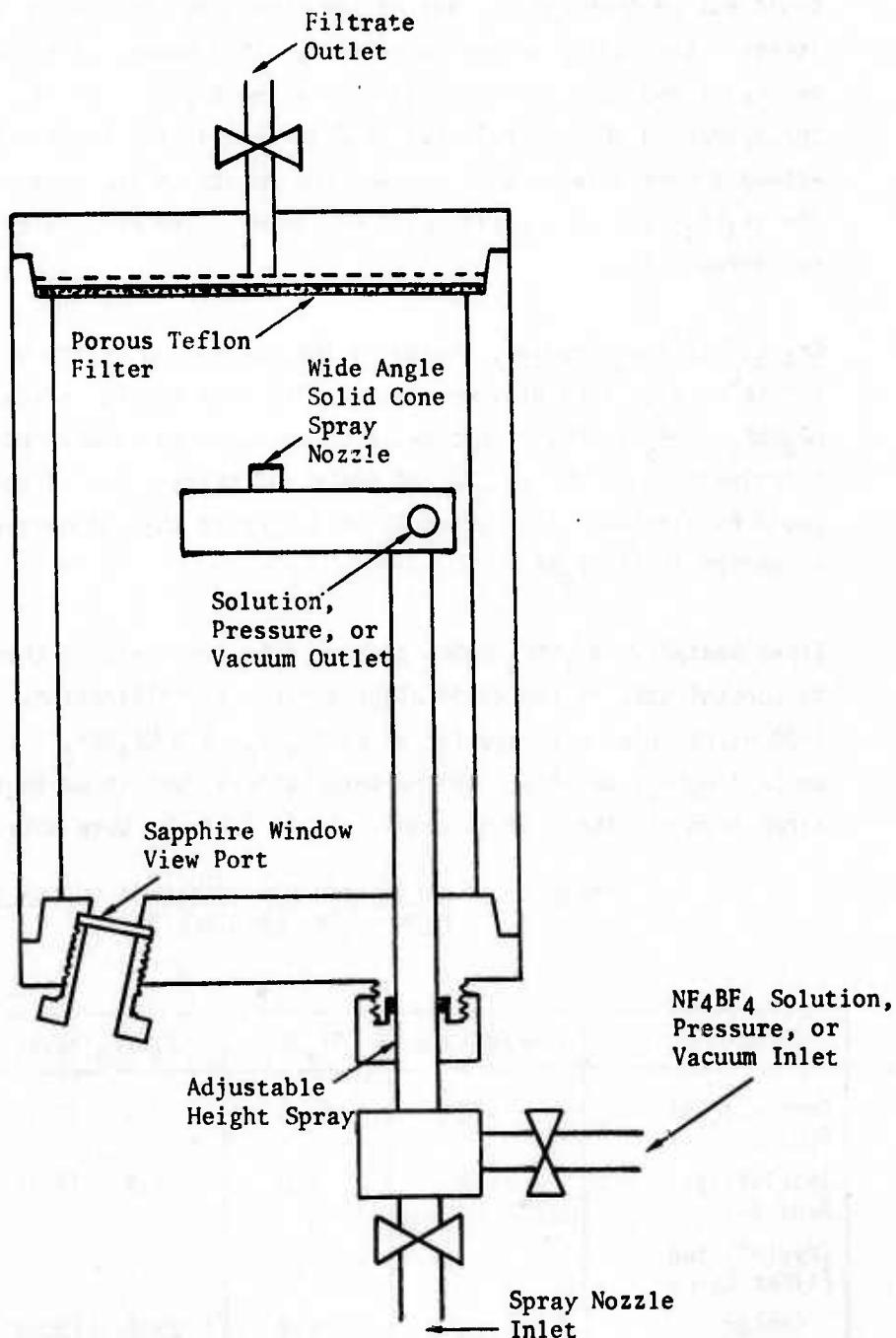


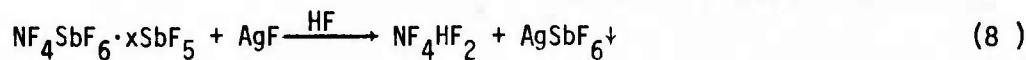
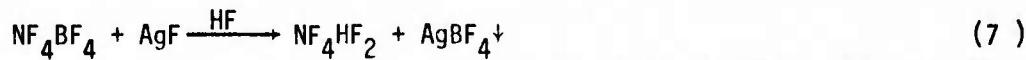
Figure 2. Teflon and Kel-F Concentrator-Crystallizer Schematic

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was sampled for analysis in two places - the center, where more efficient washing by the HF spray occurred, and the periphery. The analytical results indicated that the concentration of antimony salt in the saturated solution was too high to provide high purity  $\text{NF}_4\text{BF}_4$  by evaporation of the crystallization mother liquor. Furthermore, the higher ratio of antimony to boron  $\text{NF}_4^+$  salts in the center of the filter cake served as confirmatory evidence for the selective dissolution of the more soluble  $\text{NF}_4\text{BF}_4$  by the HF wash. Although the filtrate residue analyzed higher in  $\text{NF}_4\text{BF}_4$  content than the calculated value for the composite, this improvement in purity appeared to be due primarily to removal of the contaminating  $\text{AgBF}_4$ .

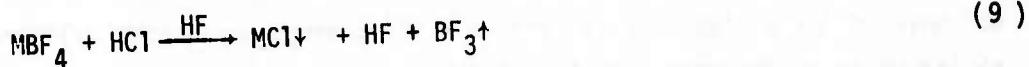
Reprocessing of Metathetical  $\text{NF}_4\text{BF}_4$ . An attempt was made to upgrade a 93 mole percent  $\text{NF}_4\text{BF}_4$  sample by using it as the starting material for the metathetical process. With the lower initial antimony content, the minimum value for antimony should be readily attained in the final product. Since the fluoro-antimonate salt is the major impurity in metathetical  $\text{NF}_4\text{BF}_4$ , a decrease in its concentration should yield a significantly purer  $\text{NF}_4\text{BF}_4$ .

In the initial step of the metathetical reaction, all  $\text{NF}_4^+$  salts (including  $\text{NF}_4\text{BF}_4$ ) were converted to the intermediate bifluoride salts (Eq. 7 and 8 ).

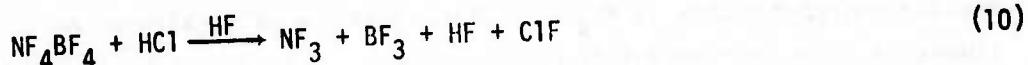


Treatment with  $\text{BF}_3$  then produced  $\text{NF}_4\text{BF}_4$  as in the process starting with the antimony salt alone. Although a 38 percent decrease in the antimony content was achieved, the purity of the  $\text{NF}_4\text{BF}_4$  recovered was unchanged at 93 mole percent due to an increase in the  $\text{AgBF}_4$  content.

HCl as a Metal Precipitant. The solubility of  $\text{AgCl}$  in HF is quite low, and presumably that of  $\text{TlCl}$  would also be low since much of chemistry and many of the physical properties of  $\text{Ag}^+$  and  $\text{Tl}^+$  compounds are parallel. The approach used to decrease the  $\text{Ag}^+$  or  $\text{Tl}^+$  content of metathetical  $\text{NF}_4\text{BF}_4$  was to saturate the HF solution of the crude  $\text{NF}_4\text{BF}_4$  with HCl in order to precipitate the metal ion without introducing other contaminants (Equation 9 ). Partial success was



attained in that the silver content of the product was decreased to about one-fourth its initial value. However, a pressure rise was noted subsequent to the HCl addition and a net loss in weight of nonvolatile solids was observed suggesting that the  $\text{NF}_4^+$  ion and HCl are incompatible. As a result of the partial loss of  $\text{NF}_4\text{BF}_4$  by the reaction postulated in Eq. 10, overall purity of the recovered



product dropped from 93 to about 90 mole percent.

Confirmation of the interaction of  $\text{NF}_4\text{BF}_4$  with HCl was obtained in a similar treatment of the  $\text{NF}_4\text{BF}_4$  prepared by metathesis using TlF in place of AgF. Although a small proportion of the thallium content of initial product was rendered insoluble, the destruction of  $\text{NF}_4\text{BF}_4$  was much more extensive suggesting that not only was HCl oxidized, but that  $\text{Tl}^+$  was also oxidized to  $\text{Tl}^{+3}$  possibly as indicated in Eq. 11. The HCl treatment decreased the purity of the  $\text{NF}_4\text{BF}_4$



from 88 to about 65 mole percent.

#### CONCLUSIONS - PHASE I, TASK 1

During Phase I, Task 1, it was possible to demonstrate that pure  $\text{NF}_4\text{BF}_4$  could be prepared by the UV-induced reaction of  $\text{NF}_3$ ,  $\text{F}_2$  and  $\text{BF}_3$  at an average rate of 1 g/hr (during short reaction times). In contrast, the metathetical reaction provided  $\text{NF}_4\text{BF}_4$  of a purity not exceeding 93 mole percent despite efforts to increase the purity by physical or chemical means. On the basis of the simplicity of the UV-induced reaction, its potential for providing the material at a lower cost and the demonstrated synthesis of pure  $\text{NF}_4\text{BF}_4$ , this method was chosen as the one to study during the scale-up task (Phase I, Task 2).

SCALE-UP OF UV PROCESS - PHASE I, TASK 2 AND  
LARGE SCALE SYNTHESIS OF  $\text{NF}_4\text{BF}_4$  - PHASE II

For the purposes of convenience and because of overlap of the experimental data, these two work efforts have been combined. During Phase I, Task 2, the objective of demonstrating a scalability of the UV process to achieve a production rate of 80 g/week of  $\text{NF}_4\text{BF}_4$  of high purity was achieved. During Phase II, this same process was used to produce 0.24 Kg of  $\text{NF}_4\text{BF}_4$  of 99 mole percent purity which was delivered on schedule.

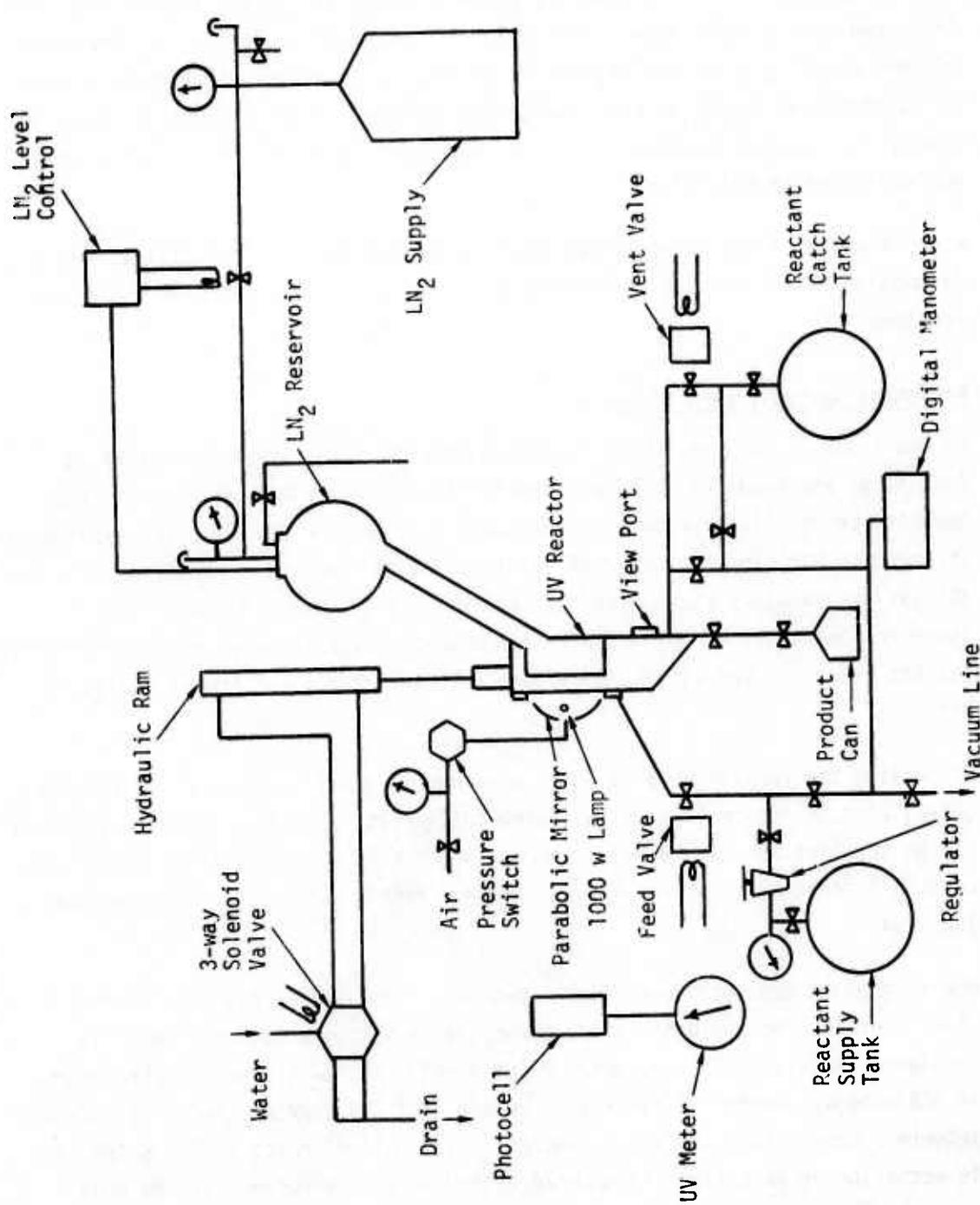
A description of the UV apparatus used to accomplish these objectives, and a discussion of the process parameters investigated are given in the following sections.

Equipment Design (Large-Scale)

On the basis of the previously described experiments conducted under Phase I, Task 1, an apparatus was designed and fabricated to produce  $\text{NF}_4\text{BF}_4$  in larger quantity and at higher rates than had been obtained in the preceding experiments. The reactor was constructed of 347 stainless steel (with the exception of a few 300 series stainless steel fittings) and was fitted with a 4-inch diameter sapphire photolysis window and a 1-inch diameter sapphire view port using Teflon gaskets. The reactor and its ancillary equipment are shown schematically in Fig. 3.

Basically, the reactor consists of a windowed chamber, to contain the reactant gases, with an internal liquid nitrogen-cooled flat photolysis surface parallel to the sapphire window. With the exception of this cooled vertical photolysis zone, all other walls of the liquid nitrogen refrigeration system are vacuum jacketed.

Reactant gases are introduced from a pressure regulated supply tank through a timer-operated, solenoid-actuated, pneumatic valve to an integral manifold supplying six 0.0135-inch diameter holes equally spaced around the perimeter of the window. Unreacted gases are vented from the reactor through a solenoid-actuated, pneumatic valve and collected in a liquid nitrogen-cooled catch tank. By actuation of an externally mounted hydraulic ram, a scraper can be made



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FIGURE 3. UV REACTOR APPARATUS SCHEMATIC

to pass over the photolysis zone to remove adhering unreacted starting materials and  $\text{NF}_4\text{BF}_4$ . The latter is collected in a removable can for transfer to the drybox. Pressures in the reactor, reactant gas feed line, and catch tank are measured with a digital manometer (Validyne, Model 56A).

The UV source is a 1000 watt, high pressure capillary mercury arc lamp (GE BH6) with appropriate air-cooling and power supply. A polished nickel parabolic reflector is positioned around the lamp to maximize the light intensity in the photolysis zone. A relative measure of the UV intensity is determined by an externally mounted photocell.

The refrigeration system consists of a 100-liter liquid nitrogen supply in series with a 14-liter constant level vessel, which permits replenishing the 100-liter supply without interruption of the photolysis process.

#### Reaction Parameters

From the experiments conducted during Task 1, the relative importance of a number of reaction parameters had been indicated. In the large-scale reactor design, an effort was made to utilize the optimum values for these parameters. However, because of the completely different geometry and partial process automation, some additional parametric factors were introduced. The study of the various process parameters was conducted under Phase I, Task 2 (Synthesis Scale-Up). During the work effort, 80g of  $\text{NF}_4\text{BF}_4$  of 99 mole percent purity was prepared and delivered to the Air Force and a production rate of 80g/week was demonstrated. These milestones were achieved even though optimization of the process was not complete by the end of this task. Therefore, the optimization studies were continued under Phase II (Large-Scale Synthesis). Even with the additional parametric evaluation, sufficient time was unavailable to obtain data which would accurately define the optimum process conditions for synthesis of  $\text{NF}_4\text{BF}_4$  in the large-scale reactor.

During the course of this investigation, it became obvious that several important variables could not be controlled and, as a result, the correlations found between reaction parameters and rate of formation of  $\text{NF}_4\text{BF}_4$  are qualitative. Insofar as it is possible, the influence on the  $\text{NF}_4\text{BF}_4$  formation rate of each of the parameters studied will be discussed. The data obtained using the

large-scale reactor are tabulated in Appendix II. Runs 1-13 were conducted under Phase I, Task 2 and Runs 14-21 under Phase II.

Effect of Temperature. Small-scale experiments indicated the essentiality of cryogenic temperatures if reasonable  $\text{NF}_4\text{BF}_4$  formation rates were to be achieved. Accordingly, only liquid nitrogen was used as a coolant in the large-scale reactor, but some temperature variation (ca. 10 C temperature rise) was accomplished by pressurization of the cooling system. A total of six runs were made with pressures of 1-1.5 atmospheres above ambient in the liquid nitrogen cooling system. No significant difference could be found between those runs made using pressurization in the cooling system and those conducted at ambient pressure. Since the latter procedure was simpler from an operational standpoint, it was the method of choice.

Effect of UV Intensity. The intensity of the UV radiation at the photolysis surface is a function of (1) the distance from lamp to the photolysis surface, and (2) the UV output of the lamp. In most experiments the lamp was positioned as close as possible (4.2 cm) to the photolysis zone. In three runs the distance was increased primarily to lower the heat load on the cooling system. Comparing runs 3 and 4 (Appendix II), the  $\text{NF}_4\text{BF}_4$  formation rate decreased more drastically than would be expected from 1.50 g/hour to 0.36 g/hour on increasing the lamp-photolysis surface distance from 4.2 cm to 6.7 cm. These data are of dubious value because of the subsequent (i.e., Run 8) observation of a significant, yet variable, build-up of  $\text{NF}_4\text{BF}_4$  in the reactor. This uncontrollable factor will be discussed in more detail (vide infra).

During the course of the series of runs, a number of lamps were used. The lamps, operated at 900 volts, exhibit a wide variation in both initial UV intensity and in aging characteristics. The observed range of initial UV intensities for ten new lamps was  $0.023\text{-}0.034 \mu\text{w/cm}^2$  (at a distance of 85 cm from the lamp) with an average value of  $0.027 \mu\text{w/cm}^2$ . When the intensity decreased to  $0.016 \mu\text{w/cm}^2$  the lamp was replaced. Lamp life varied in the range 13-45 hours (average 27.6, hours). The practice common in industry (where lower intensities are generally used) of increasing operating voltage to maintain UV intensity was impractical in our use because the accompanying much greater increase in infrared radiation added too much heat to the refrigeration load. The inherent variation of

30-50 percent in UV intensity during the life of a lamp rendered correlation of  $\text{NF}_4\text{BF}_4$  formation rate with other given reaction parameters qualitative.

Effect of Reactant Mole Ratios. In view of the fact that  $\text{NF}_4\text{BF}_4$  is formed from an equimolar mixture of  $\text{NF}_3$ ,  $\text{BF}_3$  and  $\text{F}_2$ , it was logical to use such a mixture as the starting material in the UV process. No attempt was made to determine the ratio of the starting materials contained in the reactor in "dynamic equilibrium" during the course of a run.

Effect of Mode of Introduction of Reactants. The intermittent mode of addition of the equimolar  $\text{NF}_3\text{-BF}_3\text{-F}_2$  reactant mixture was dictated by the results of the small-scale experiments. To optimize the process, it would be necessary to achieve a balance between a high  $\text{NF}_4\text{BF}_4$  formation rate with low conversion or a low  $\text{NF}_4\text{BF}_4$  formation rate with high conversion. Theoretically, a high formation rate should be achieved by frequent renewal of the reactants in the photolysis zone and high conversion by infrequent renewal. The quantity of reactants introduced with each increment must not exceed that which can be converted to products in the time between additions, or both  $\text{NF}_4\text{BF}_4$  formation rate and conversion will be low.

Comparison of Run 19 with combined Runs 9 and 10 (each of which has approximately the same reactant feed rate, see Appendix II) suggests that doubling the quantity of reactants per increment added and halving the frequency of additions resulted in a 20 percent increase in the  $\text{NF}_4\text{BF}_4$  formation rate. Further decreases in the frequency of addition resulted in very significant lowering of the  $\text{NF}_4\text{BF}_4$  formation rate (Runs 20 and 21). An insufficient number of runs of long duration (12-35 hours) were made to define either the frequency of incremental additions or the optimum quantity of reagents introduced per addition. Such data as were obtained are qualitative due primarily to two uncontrolled parameters inherent in the reactor design. These parameters are discussed below.

Effects of Reactor Hold-up of  $\text{NF}_4\text{BF}_4$  and Reactant Gas Orifice Plugging. The nature of the  $\text{NF}_4\text{BF}_4$  produced by the UV process is such that the dry powder is not free-flowing. Its angle of repose approaches the vertical. Accordingly, an average of about 5 grams of product accumulated on the 40-degree slope of the reactor bottom before additional product falling from the scraper blade would

slide into the collection can. Temperature cycling between runs sometimes dislodged large flakes of product from the photolysis surface which facilitated the accumulation of product (up to 20 grams) in the reactor or complete plugging of the outlet. In any case, the quantity of  $\text{NF}_4\text{BF}_4$  which accumulated in the reactor was a very substantial, yet variable, percentage of the total produced in all runs. In some runs mechanical removal of product resulted in more reliable formation rate data. The behavior of  $\text{NF}_4\text{BF}_4$  is postulated to be the result not only of the irregular shape of the solid particles which readily acquire an electrostatic charge, but more importantly, the extremely high HF solubility of the product. A small amount of HF introduced with the  $\text{F}_2$ , or from trace hydrolysis of  $\text{BF}_3$  by atmospheric moisture leaking into the reactor is suspected to promote the observed stickiness and slight caking of the product.

During 75-100 hours of operation, the quantity of reactant gases introduced per increment was observed to decrease to about one-half its initial value as measured by the maximum pressure rise immediately after the addition. This decrease in addition rate of reactants was found to be due to an uneven accumulation of solids in the inlet orifices. Thus, not only did the amount of reactants introduced decrease (at a given pressure differential between reactant feed supply and reactor and a given open valve time), but the distribution of condensed reactants on the photolysis surface became uneven. The result was that correlations of  $\text{NF}_4\text{BF}_4$  formation rate with incremental reactant feed rates are qualitative in most instances.

Process Efficiency. During the 34-hour run time of Run 19 (Appendix II), the pressure in the 9.5 liter reactant supply tank decreased by 75 psig which is equivalent to 0.66 mole (117 g)  $\text{NF}_4\text{BF}_4$ . The 98.9g  $\text{NF}_4\text{BF}_4$  synthesized indicated an 84 percent conversion of starting materials to product. Assuming the feed rate in Run 21 to be one-half of that of Run 19, the conversion is calculated to be 97 percent.

Overall conversion for all twenty-one runs is calculated to be 31 percent since 369g  $\text{NF}_4\text{BF}_4$  (323g delivered, 46g analytical samples, mechanical losses, or discarded as partially hydrolyzed) was prepared from the 1197g of an equimolar mixture of  $\text{NF}_3\text{-BF}_3\text{-F}_2$ .

## EXPERIMENTAL

### REAGENTS

#### HF Drying

A 12-1b quantity of commercial anhydrous HF (Matheson) was transferred into an evacuated 9.5 l stainless steel, high pressure cylinder fitted with a 1000 psi pressure gage. After cooling to -78 C, approximately 500 mm of non-condensable gas was pumped off. A 500 ml cylinder containing approximately 40 l F<sub>2</sub> at -196 C was then connected to the HF cylinder and, after allowing both cylinders to warm to ambient temperature, the HF was pressurized with F<sub>2</sub> to 100 psi. The F<sub>2</sub> pressure over the HF dropped to 85 psi after standing overnight and remained constant during 1 hour shaking of the HF cylinder. The unused F<sub>2</sub> and O<sub>2</sub> which had been generated were condensed at -196 C in the 500 ml cylinder which was then disconnected. The residual F<sub>2</sub>-O<sub>2</sub> mixture was removed from the HF by vacuum pumping for about 3 hrs at -78 C, and then briefly at ambient temperature.

#### NF<sub>3</sub>

NF<sub>3</sub> was obtained from the Rocketdyne plant where it is prepared by electrolysis of NH<sub>4</sub>HF<sub>2</sub>. Analysis of this material indicated the following composition.

Component	w/o
NF <sub>3</sub>	99.5
N <sub>2</sub>	0.3
HF	0.1
CF <sub>4</sub>	trace < 0.01
N <sub>2</sub> O	trace < 0.01
trans-N <sub>2</sub> F <sub>2</sub>	trace < 0.01
cis-N <sub>2</sub> F <sub>2</sub>	not detectable
F <sub>2</sub>	not detectable

### SbF<sub>5</sub>

Commercial SbF<sub>5</sub> (Ozark-Mahoning) was distilled at atmospheric pressure under dry nitrogen from glass apparatus into Teflon bottles. Only the center cut (b.p. 148 C) was taken for use, and the liquid was subsequently stored and transferred entirely within a drybox.

All other chemicals were obtained commercially and used as received unless otherwise noted.

### UV PROCESS

#### Small-Scale UV Experiments

The pre-photolysis procedure generally used to prepare NF<sub>4</sub>BF<sub>4</sub> on a small-scale by the UV process was as follows. A part (or all when smaller amounts were used) of the F<sub>2</sub> was introduced at -196 C into an evacuated reaction vessel. The UV lamp was then turned on to permit the system to reach thermal equilibrium (5 to 10 minutes). Measured amounts of NF<sub>3</sub> and BF<sub>3</sub> (either premixed or separately) were then quickly introduced by using pressures higher than the internal F<sub>2</sub> pressure. Additional F<sub>2</sub>, if necessary, was then added. Deviations from this procedure are noted in Appendix I for individual experiments.

Unless otherwise noted in Appendix I, the procedure for continuous or intermittent addition of reagents differed only in that, after introducing part of the reactants, the flow of the remaining gases into the reactor was either (1) controlled with a needle valve and monitored by pressure measurements, or (2) by rapid addition at varying times during photolysis. Details of individual experiments are given in Appendix I.

#### Large-Scale UV Preparations

Operation of the large-scale UV-reactor employed the following procedure. An equimolar mixture of NF<sub>3</sub>/BF<sub>3</sub>/F<sub>2</sub> was introduced into the evacuated photolysis cell, which was cooled on the internal working face to -196 C, until the pressure (F<sub>2</sub> partial pressure) rose to the preselected working range (~500 mm). The UV lamp was turned on and the feed cycle timer circuit was activated to admit

additional incremental amounts of the equimolar gas mixture from a pressure regulated supply. The reactant gas feed rate was governed by the time that the solenoid activated pneumatic inlet valve was open, the pressure differential between the reactor and supply, and the time between inlet valve activations. At approximately 15 minute intervals, a hydraulic ram was manually activated to drive a scraper blade across the internal working face of the reactor and thereby dislodge the mixture of  $\text{NF}_4\text{BF}_4$  and unreacted starting materials. The unreacted starting materials volatilized and the increase in cell pressure was reduced to the preselected value by bleeding the unreacted materials into a catch tank at -196 C. The solid product was deposited in a doubly-valved removable collection vessel under the photolysis cell. At the conclusion of a run, the bulk of the liquid nitrogen refrigerant was pressure-transferred from the apparatus. As soon as the refrigerant was depleted, the cell pressure began to rise and the feed cycle timer circuit was deactivated. The pressure in the photolysis cell was maintained just below atmospheric by controlled release of the volatilized unreacted gases to the catch tank. The lamp was turned off when the pressure stabilized. The product collection vessel was then evacuated and transferred to a drybox to remove the product. Details for individual runs are tabulated in Appendix II.

#### METATHETICAL PROCESS

##### Attempted Analysis for Water in HF Solution

A sample of  $\text{F}_2$ -dried HF was added to an evacuated, tared Teflon tube containing 5  $\mu\text{l}$   $\text{H}_2\text{O}$ . The weighed solution was then partitioned in an evacuated system into three analytical samples by pouring part of it into two other tared Teflon tubes. The three samples were in turn allowed to react with an excess of  $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$  in HF solution. The  $\text{NF}_3$  generated was pumped through a -196 C trap into a -210 C trap and then warmed and expanded into an IR cell of known volume. The amount of  $\text{NF}_3$  was calculated from the measured absorbance of the  $907 \text{ cm}^{-1}$  band which had been calibrated against known  $\text{NF}_3$  pressures. A fourth experiment was conducted and the  $\text{NF}_3$  was pumped through a -126 C trap into the -210 C trap without significant change in the amount of  $\text{NF}_3$  obtained. A result comparable to those obtained using water was obtained when the salt,  $\text{OH}_3\text{SbF}_6$ , was used as the water source.

### Solubility and Density of HF Solutions of $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$

A 0.2345g sample of  $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$  was dissolved in HF at ambient temperature in a Teflon ampoule fitted with a Teflon valve. The solvent was removed under vacuum to leave a solid which weighed 0.2363g after pumping for 1 hr at ambient temperature. In an independent experiment, approximately 3g of  $\text{NF}_4\text{SbF}_6 \cdot 0.8\text{SbF}_5$  was dissolved in HF at ambient temperature in a Teflon ampoule equipped with a Teflon filter and valve. After filtering out Monel chips and the relatively insoluble  $\text{M}(\text{SbF}_6 \cdot x\text{SbF}_5)_2$  salts ( $\text{M} = \text{Cu, Ni}$ ), the filtrate was observed to be just slightly turbid in a second tared, volume-calibrated Teflon ampoule. HF was gradually pumped away and crystallization of the salt was induced by supercooling the ampoule tip. The slurry was allowed to warm slowly with agitation in a water bath, the temperature of which was measured with an Anshutz thermometer. The temperature at which the last crystal dissolved was noted as was the volume of the solution. The solution weight was subsequently determined at ambient temperature. The weight of dissolved salt was determined by complete removal of solvent under the conditions described above.

### $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ Preparative Studies

A typical preparation of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  (Run 16, Table 9) was conducted as follows. A 1000 ml Monel high pressure (3500 psi) cylinder was charged with 602g (2.78 moles)  $\text{SbF}_5$  in a drybox. After fitting the cylinder with a Monel pressure gage and valve, 167g (2.35 moles)  $\text{NF}_3$  and 98.1g (2.58 moles)  $\text{F}_2$  were condensed in the cylinder at -196 C. When the mixture had warmed to ambient temperature (pressure 1600 psi), the cylinder was placed in a 115 C oven for 24 hrs. The pressure was observed to be 2550 psi (after 4.5 hrs in oven) and 1900 psi (1125 psi at ambient temperature) as it was removed from the oven. The unreacted  $\text{NF}_3\text{-F}_2$  mixture (149 g) was removed from the cylinder at ambient temperature and recovered for reuse. Infra-red analysis of the recovered  $\text{NF}_3\text{-F}_2$  mixture indicated that the mole ratio  $\text{NF}_3/\text{F}_2$  remained in the range 1.0-1.1.

The crude product was pyrolyzed under dynamic vacuum in a 200 C oven for 24 hrs and excess  $\text{SbF}_5$  (204 g) was distilled through an electrically heated line to a -78 C trap for recovery and subsequent reuse. A 100 ml quantity of

TABLE 9.  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  PREPARATIONS

Run No.	$\text{NF}_3$ , Moles	$\text{F}_2$ , Moles	$\text{SbF}_5^*$ Moles	Temp., $^{\circ}\text{C}$	Reactor Time, hrs	$\text{Sb}/\text{N}$ <sup>(a)</sup> Initial Final	Pyrolysis Time, hrs	Product Wt., g Crude HF Sol. HF Insol.	(b) (b) (b) (b) (b) (b) (b) (b) (b)
1	1.96	2.14	2.05	115	29	3.73	1.83	90	280 (b)
2	1.94	2.16	2.04	115	70	3.71	2.05	40	305 (b)
3	1.97	2.01	2.03	115	25.5	4.17	2.25	40+ <sup>(c)</sup>	288 (b)
4	1.80	1.98	1.92	115	54	3.74	1.80	51	257 (b)
5	2.01	2.18	2.27	115	24	3.37	1.67	48+ <sup>(c)</sup>	315 (b)
6	2.13	2.40	2.44	115	69	3.14	1.84	72	397 (b)
7	2.17	2.41	2.16	200	5	3.93	1.87	48	283 260 (e) 14
8	2.17	2.41	2.15	200	21.5	3.61	[2.02] <sup>(d)</sup>	44	189 32 (e) 153
9	1.90	2.13	2.12	250	5	3.35	1.99	48	342 298 38
10	1.85	2.05	2.10	250	24	2.87	2.06	.44	398 360 35
11	2.31	2.59	2.79	115	23	3.40	2.06	44	450 430 21
12	2.29	2.56	2.78	115	22	3.19	2.10	44	493 -- --
13	2.32	2.61	2.72	115	22	3.01	1.92	24	481 -- --
14	2.38	2.61	2.73	115	24	2.78	1.89	17+ <sup>(f)</sup>	510 -- --
15	2.33	2.60	2.89	115	23.5	3.00	1.99	28	520 -- --
16	2.35	2.58	2.78	115	24	2.88	1.91	24	503 -- --
17	2.35	2.58	2.79	115	24	2.71	1.93	25	542 -- --

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(a) Before and after recovery of excess  $\text{SbF}_5$  by 24-48 hour pyrolysis at 200 C.

(b) These preparations, made prior to this contract, were isolated mechanically rather than by HF extraction.

(c) Exact pyrolysis time unknown due to plugging of  $\text{SbF}_5$  outlet.

(d) During further heating, temperature control failed resulting in a temperature excursion and extensive decomposition of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ .

(e) The major portion of this material may have passed through filter as finely divided solid.

(f) Exact pyrolysis time unknown due to power failure while unattended.

$F_2$ -dried HF was added to the 503 g of crude product in the cylinder, and the mixture was mechanically shaken for 1 hr. The resulting slurry of copper and nickel salts was pressurized to 50 psi with nitrogen and pneumatically transferred to a 1070 ml Teflon container equipped with a Teflon filter. The slurry was pressure-filtered into a second Teflon container from which the filtrate was used directly in a metathetical reaction with  $AgF$ . After vacuum pumping the solvent from the first Teflon container, the weight of the copper and nickel salts was found to be 12 g.

$NF_4SbF_6 \cdot xSbF_5$  Metathesis to  $NF_4BF_4$

Compatibility of  $Tl^+$  with  $NF_4^+$ . A preliminary experiment involving the first reaction step of the metathetical process, and conducted in Teflon tubing reactors, was not completely satisfactory in that mechanical hold-up of the  $TlF$ -HF solution prevented using an excess of this reagent compared to the amount of  $NF_4SbF_6 \cdot 0.8SbF_5$ . On adding one-half to three-quarters of the 1.35 ml  $TlF$ -HF solution (containing 2.188g or 9.82 mmoles  $TlF$ ) to 1.76 ml of a HF solution of  $NF_4SbF_6 \cdot 0.8SbF_5$  (containing 2.645g  $NF_4SbF_6 \cdot 0.8SbF_5$  or 9.62 mg-at Sb), a colorless precipitate formed immediately. After 0.5 hour at ambient temperature,  $NF_3$  (0.44 cc) was collected and determined by infrared spectroscopy to be equivalent to 0.36% of the  $NF_4^+$ . After standing at ambient temperature for 6 days, an additional 0.15% of the  $NF_4^+$  was found as  $NF_3$ , suggesting that the observed precipitate was  $TlSbF_6$  which is stable toward oxidation by  $NF_4^+$ .

Metathesis Using  $TlF$ . Large-scale reactions were conducted in the metathetical reactor shown in Fig. 1. This reactor is entirely constructed of Teflon and Kel-F including reaction vessels, valves, filters, pressure relief valve (set at 60 psi) and diaphragm pressure gage.

An approximately 0.2 mole scale preparation of  $NF_4BF_4$  was made using  $TlF$  as the precipitant for  $SbF_6^-$ . A solution of 100 g (0.45 mole) of  $TlF$  in 72 g HF was added to a solution of 103 g (0.208 mole) of 89.2%  $NF_4SbF_6 \cdot 0.53 SbF_5$  (Run 9, Table 9) in 44 g HF. The resulting slurry was filtered to remove  $TlSbF_6$ , which was washed with 25 g HF. The combined filtrate and washings were saturated with  $BF_3$  (19 g, 0.28 mole) to 20 psig. The resulting  $TlBF_4$  was filtered, and the filtrate was evaporated to dryness under vacuum. All of the above operations were conducted in the metathetical reactor.

Analyses of the 38.2 g of crude product were performed by hydrolyzing the product on a vacuum line. The  $\text{NF}_3$  evolved was estimated by the IR technique. The hydrolyzate was then analyzed for B, Tl, Sb, Ni and Cu by atomic absorption spectrometry. A 0.2660 sample of the product on analysis gave: B, 13.8 mg; Tl, 54.4 mg; Sb, 6.4 mg; Ni, 0.006 mg; and Cu, 0.003 mg. Two samples, 0.0027 g and 0.0094 g, gave on an equivalent basis  $\text{NF}_3$  values of 93 mg and 47.5 mg, respectively.

Metathesis Using  $\text{AgF}$ . For a typical reaction, 300 g  $\text{AgF}$  was dried in a vacuum oven at 60°C for 4 hrs. The resulting 292.6 g  $\text{AgF}$ , after transfer to a 1070 ml Teflon container in the drybox, was dissolved in 400 ml of  $\text{F}_2$ -dried HF and pressure-filtered (20 psi  $\text{N}_2$ ) into a second Teflon container to remove 14 g of insolubles. The resulting HF solution contained approximately 279 g (2.20 moles)  $\text{AgF}$ .

A HF solution of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  was prepared as indicated (vide supra). Although not analyzed, the solution was estimated to contain approximately  $488 \pm 3$  g of 95-96 mole percent  $\text{NF}_4\text{SbF}_6 \cdot 0.9 \text{SbF}_5$  (ca. 1.8 g-atom Sb) on the basis of other analyses (cf. Tables 6 and 9).

The 583 g of  $\text{NF}_4\text{SbF}_6 \cdot 0.9 \text{SbF}_5$  solution was transferred rapidly under 25 psi  $\text{N}_2$  pressure into the  $\text{AgF}$  solution, which had been cooled for 0.5 hr in an ice bath. After standing in the ice bath for an additional 0.5 hr, the slurry was pressure-filtered to remove  $\text{AgSbF}_6$  which was then washed quickly with 150 ml HF. The nitrogen in the system was pumped away from the combined filtrate and washings, and gaseous  $\text{BF}_3$  (95 g, 1.4 moles) was then added, with moderate shaking during 0.5 hr, until the pressure increased to 20 psi. The resulting slurry was filtered to remove  $\text{AgBF}_4$ , and the filter cake was washed quickly with 50 ml HF. The solvent HF was vacuum pumped from the  $\text{NF}_4\text{BF}_4$  solution, as well as from the solid  $\text{AgSbF}_6$  and  $\text{AgBF}_4$  co-products, during 9 hrs. The weights of the isolated products were  $\text{NF}_4\text{BF}_4$  185 g,  $\text{AgSbF}_6$  534 g, and  $\text{AgBF}_4$  88 g.

A 0.3689 g sample of  $\text{NF}_4\text{BF}_4$  was hydrolyzed in a Teflon ampoule on the vacuum line using approximately 1.5 ml  $\text{H}_2\text{O}$ . The colorless solid turned black as

the ice began to sublime, suggesting the oxidation of Ag(I) to Ag(II). The solid foamed vigorously on contact with liquid water to give a black solution (or colloidal suspension), which changed first to a pink solution and then colorless during 0.5-1.0 hr. The resulting  $\text{NF}_3$  (37.40 cc) and  $\text{O}_2$  (18.55 cc) were separated by condensation of the  $\text{NF}_3$  at -210°C ( $\text{N}_2$  slush), and collected separately by means of a Sprengel pump system. The observed  $\text{NF}_3/\text{O}_2$  of 2.02 compared very favorably with the theoretical ratio of 2. The hydrolyzate was analyzed by atomic absorption spectroscopy. Found: B, 19.1 mg; Sb, 33.2 mg; Ag, 7.95 mg; Cu, 0.009 mg; Ni, 0.012 mg. On the basis of these analyses, the  $\text{NF}_4\text{BF}_4$  was approximately 83 mole percent pure, and was obtained in about 89 percent yield based on the  $\text{NF}_4\text{SbF}_6 \cdot 0.9\text{SbF}_5$  used.

Reprocessing of Metathetical  $\text{NF}_4\text{BF}_4$ . The typical metathesis reaction was run in the usual manner using 93 mole percent  $\text{NF}_4\text{BF}_4$  as the  $\text{NF}_4^+$  source rather than  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ . After the metathesis with  $\text{AgF}$ , the slurry was cooled in a -78°C bath (rather than the usual 0°C bath) for 1.75 hrs before filtration of the  $\text{AgBF}_4\text{-AgSbF}_6$  mixture from the  $\text{NF}_4\text{HF}_2$  solution. The filtrate was saturated with  $\text{BF}_3$  and the  $\text{AgBF}_4$  was filtered. The  $\text{NF}_4\text{BF}_4$  isolated from the filtrate, by removal of HF under vacuum, was analyzed hydrolytically. A 0.3357 g analytical sample gave 38.2 cc  $\text{NF}_3$ , 18.0 mg B, 14.8 mg Sb, and 4.91 mg Ag. From these data, the calculated composition of the product (in mole percent) was 93.0  $\text{NF}_4\text{BF}_4$ , 4.6  $\text{NF}_4\text{SbF}_6 \cdot 0.51\text{SbF}_5$ , and 2.6  $\text{AgBF}_4$ .

HCl As a Metal Precipitant. A 29 g sample of  $\text{NF}_4\text{BF}_4$  (93 mole percent purity), was dissolved in 23 g HF in a Teflon container which was then pressurized to 10 psi with HCl (3 g). The pressure rose to 15 psi on standing at ambient temperature for 5 minutes, after which time the mixture was filtered to remove 0.70 g  $\text{AgCl}$ . The solvent was removed from the filter cake and filtrate under vacuum, and 28 g of HF-soluble, nonvolatile products was recovered. A 0.3446 g sample of the recovered  $\text{NF}_4\text{BF}_4$  was analyzed and 38.24 cc  $\text{NF}_3$ , 18.9 mg B, 17.1 mg Sb, and 1.61 mg Ag were obtained after hydrolysis. These values indicated a reduction in purity of the  $\text{NF}_4\text{BF}_4$  to 90 mole percent.

A 36 g  $\text{NF}_4\text{BF}_4$  sample of 88 mole percent purity and prepared by use of  $\text{TiF}_4$ , was dissolved in 19 g HF and treated with 2.5 g HCl in the same manner as described above. A pressure rise to 12 psi was observed, and only 30 g of

HF-soluble, non-volatile products were recovered after filtration and vacuum drying of the filtrate. The precipitate,  $TlCl$  (or  $TlCl_3$ ), weighed 5 g. A 0.3384 g sample gave on hydrolysis 28.53 cc  $NF_3$ , 15.7 mg B, 11.1 mg, and 62.0 mg Tl. The purity of the treated  $NF_4BF_4$  was reduced to about 65 mole percent.

#### Purification of $NF_4BF_4$ by Crystallization

Three analyzed batches of crude  $NF_4BF_4$  were combined and the resulting composite (470 g) was dissolved in 490 g HF in a Teflon vessel. The resulting solution was filtered and transferred to the Teflon and Kel-F Crystallizer (Fig. 2) where it was observed through a sapphire window to be a colorless, clear solution. The residual material (23 g) remaining on the filter was primarily the relatively insoluble  $AgBF_4$  (see Table 10).

Crystallization of  $NF_4BF_4$  from the filtrate (929 g) was initiated by removal of HF under reduced pressure. After pumping for about 0.3 hr, crystals (presumably  $AgBF_4$  or possibly  $AgSbF_6$ ) had formed and continued to form slowly as 303 g HF was removed during 4.8 hours. At this point, the cold solution changed rapidly to a thick slurry of crystals (presumed to be  $NF_4BF_4$  but possibly  $NF_4SbF_6 \cdot xSbF_5$ ) which redissolved during 0.75 hr as the mixture warmed to ambient temperature without further removal of HF. An additional 95 g HF (total 398 g) was removed during 2.2 hours after which the crystallizer was inverted to transfer the slurry onto the filter. The vapor pressure over the slurry was  $19.3 \pm 1.0$  inches vacuum ( $270 \pm 25$  mm) at 20 C. After cooling the upper portion of the apparatus for several hours at 2-5 C, the slurry was pressure-filtered under 8 psig  $GN_2$ . The filter cake was spray-washed with 20 ml HF at ambient temperature under 30 psig  $GN_2$  (flow rate 555 ml/min), and the washings were combined with the mother liquor. Both the filter cake and filtrate were pumped to dryness, weighed and analyzed (see Table 10). A material balance indicated that 17 g of the solids introduced were lost by conversion to volatile products.

TABLE 10. ANALYSES OF CRYSTALLIZED  $\text{NF}_4\text{BF}_4$ 

	Runs 9-11, HF Insolubles	Crystallized Filter Cake		Filtrate Residue
		Center	Periphery	
Sample Size, g	1.0119	0.3530	0.4259	0.3654
Found, mg				
$\text{NF}_3$ (cc)	--	31.65	38.31	41.42
B	49.8	9.9	12.8	18.8
Sb	23.3	83.8	92.5	28.4
Ag	471	4.8	7.9	2.23
Cu	0.075	0.009	0.009	0.012
Ni	0.185	0.005	0.003	0.001

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## CONCLUSIONS AND RECOMMENDATIONS

The UV-induced synthesis of  $\text{NF}_4\text{BF}_4$  from  $\text{NF}_3$ ,  $\text{BF}_3$  and  $\text{F}_2$  has been developed from a batch process producing milligram quantities to a continuous process producing 2.90 g/hour of 99 mole percent purity with an 84 percent conversion of reactants to product. The process has not yet been optimized because insufficient time was available to complete the parametric investigation. Despite the lack of process optimization, approximately 0.32 Kg of 99 mole percent pure  $\text{NF}_4\text{BF}_4$  was prepared and delivered to the Air Force on schedule.

For further development work on a solid propellant fluorine generator requiring completely gaseous non-deactivating exhaust products, it is recommended that  $\text{NF}_4\text{BF}_4$  produced by the UV process be procured on a supply contract. At the present stage of development 100g  $\text{NF}_4\text{BF}_4$  per week (40 hours) can be produced and obviously this rate could be increased to 300 g/week with a continuous operation. Extrapolation of data used for the design of the process equipment suggests that the  $\text{NF}_4\text{BF}_4$  production rate could be doubled without changes in the existing equipment. During the course of a supply contract additional runs would be made with increased reactant feed rates to verify this postulate and subsequently optimize the production rate and conversion.

Alternatively, for development work on a solid propellant fluorine generator where formation of a clinker is permissible, utilization of  $\text{NF}_4\text{BF}_4$  as the oxidizer would be highly advantageous in that the lower formula weight (relative to other  $\text{NF}_4^+$  sources) provides a larger proportion of available  $\text{F}_2$  per pound of oxidizer. For this application it is recommended that  $\text{NF}_4\text{BF}_4$  produced by either the UV process or the metathetical process should be utilized. At the present stage of development metathetical  $\text{NF}_4\text{BF}_4$  (93 mole percent or 84 weight percent) can be produced at the rate of 150 g/week (40 hours). Experience gained on this contract suggests that 300 g/week can be prepared without changes in the existing equipment.

## REFERENCES

1. K. O. Christe, R. D. Wilson and A. E. Axworthy. Inorg. Chem., 12, 2478 (1973).
2. W. E. Tolberg et al., AFRPL-TR-68-47, "Synthesis of Energetic Oxidizers," Stanford Research Institute, Menlo Park, California, 28 March 1968 (CONFIDENTIAL - Declassified 31 December 1974).
3. Rocketdyne, unpublished.
4. C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner and J. N. Wilson, Inorg. Chem. 11, 1696 (1972).
5. S. M. Sinel'nikov and V. Ya. Rosolovskii, Dokl. Akad. Nauk SSSR, 194, 1341 (1970).
6. V. Ya. Rosolovskii, V. I. Nefedov and S. M. Sinel'nikov, Izv. Akad. Nauk SSSR, Ser. Khim., 7, 1445 (1973).
7. E. Safary, J. Romand and B. Vodar, J. Chem. Phys., 19, 379 (1951).
8. K. O. Christe, C. J. Schack and R. D. Wilson, to be published in Inorg. Chem., 14 (September 1975).
9. A. F. Clifford and S. Kongpricha, J. Inorg. Nucl. Chem., 20, 147 (1961).

## APPENDIX I. SMALL SCALE UV EXPERIMENTS

Expt. No.	Reaction Temp., °C	Photolysis Time, hrs.	Mole Ratio BF <sub>3</sub> / NF <sub>3</sub>	Total F <sub>2</sub> Used, cc	Reactant Addition Amounts	Addition Mode (a)	Reactant Addition Times (min)	Pressure Range (during photolysis), mm	Reactor Used (b)	Lamp to Condenser Distance (c), cm	UV Lamp Type (d)	NF <sub>4</sub> BF <sub>4</sub> Weight mg	NF <sub>4</sub> BF <sub>4</sub> Method (e)	Average NF <sub>4</sub> BF <sub>4</sub> Formation Rate, mg/hr
1	amb.	18	1	54	8	-	-	~650 (f)	TS	27	H(A)	0	v	0
16	amb.	0.08	1	128	B	-	-	(105 ps) 9 (~1000)	TS	7	H(A)	0	v	0
6	amb.	5	1	1 (9)	131	B	-	700-690	TS	27	H(A)	0	v	0
5	-78	42	1	2 (9)	250	B	-	958-926	TS	27	H(A)	trace	trace	trace
2	amb.	15.5	1	9	161	B	-	undetermined	TS	27	H(A)	trace	v	trace
54	-196	7.5	1	2.2	161	B	-	978-950	TS	27	H(A)	trace	v	trace
3	amb.	16.5	1	14	10	B	-	158 ± 10	TS	27	H(A)	0	v	0
7	-196	64	1	2 (9)	140	B	-	968-948	TS	27	H(A)	95	v	6
7	-196	64	1	2 (9)	140	B	-	170 ± 10	SSS-8	25	H(A)	0	v	0
8	amb.	16	1	1	140	B	-	978-966	SSS-8	25	H(A)	33	v	3.5
9	amb.	9.5	1	2	372	B	-	135-115	undetermined	25	H(A)	0	v	0
17	amb.	16	1	0.5	300	B	-	>31 ps 19 (~)	undetermined	25	H(A)	120	v	15
17	amb.	10	1	0.5	300	B	-	undetermined	undetermined	0	H(A)	0	v	0
13	-196	2	3.3	0.9	180	1	100 NF <sub>3</sub> + 400 BF <sub>3</sub> + 80 F <sub>2</sub>	undetermined	SB	12	H(A)	0	v	3.5
14	-140 ± 7	2	1.1	0.25	150	1	100 NF <sub>3</sub> + 650 BF <sub>3</sub> + 50 F <sub>2</sub>	undetermined	SB	12	H(A)	3.5	v	1.7
12	-186	8	1	2	140	B	50 NF <sub>3</sub> (30 intervals)	50 F <sub>2</sub> (30 intervals)	TS	27	H(A)	64	v	8
55	-186	2	1	0.83	1000	B	10% F <sub>2</sub> added before NF <sub>3</sub> +BF <sub>3</sub>	370-350	SB	12	H(A)	69	v	34.5
54	-186	2	1	0.50	600	B	17% F <sub>2</sub> added before NF <sub>3</sub> +BF <sub>3</sub>	260-230	SB	12	H(A)	75	v	37.5
53	-186	2	1	0.33	400	B	25% F <sub>2</sub> added before NF <sub>3</sub> +BF <sub>3</sub>	225-150	SB	12	H(A)	69	v	34.5
52	-186	2	1	0.17	200	8	-	230-125	SB	12	H(A)	71	v	35.5
50	-186	2	1	0.17	200	B	-	275-115	SB	12	H(A)	76	v	35.5
51	-186	2	1	0.08	100	B	-	150-60	SB	12	H(A)	71	v	35.5
18	-196	2	0.21	0.14	200	1	1000 NF <sub>3</sub> + 100 BF <sub>3</sub> + 66 F <sub>2</sub>	60-40	SB	12	H(A)	49	v	24.5
19	-196	2	0.21	0.29	400	1	(initially); 4 x 33 F <sub>2</sub> (25 intervals)	2 x 200 NF <sub>3</sub> (45 intervals)	TS	27	H(A)	64	v	8
20	-196	2.5	0.21	0.21	300	1	1000 premixed NF <sub>3</sub> /BF <sub>3</sub> = 14/3 + 200 F <sub>2</sub>	2 x 100 BF <sub>3</sub> (30 intervals)	SB	12	H(A)	10 <sup>(1)</sup>	v	-
							(initially); 3 x 100 NF <sub>3</sub> /BF <sub>3</sub> and 5 x 50 NF <sub>3</sub> /BF <sub>3</sub> (10-15 intervals)	2 x 100 F <sub>2</sub> (30 intervals)	SSS-3	12	H(A)	0	v	0
							(initially); NF <sub>3</sub> /BF <sub>3</sub> = 14/3 + 200 F <sub>2</sub>	1700 premixed NF <sub>3</sub> /BF <sub>3</sub> = 14/3 + 200 F <sub>2</sub>					v	0

54	-186	2	1	0.50	600	B	17% F <sub>2</sub> added before NF <sub>3</sub> -BF <sub>3</sub>	260-230	SB	12	H(A)	75	6	37.5		
53	-186	2	1	0.33	400	B	25% F <sub>2</sub> added before NF <sub>3</sub> -BF <sub>3</sub>	225-150	SB	12	H(A)	69	6	34.5		
52	-186	2	1	0.17	200	B	-	230-125	SB	12	H(A)	71	6	35.5		
50	-186	2	1	0.17	200	B	-	275-115	SB	12	H(A)	76	6	38		
51	-186	2	1	0.08	100	B	-	150-60	SB	12	H(A)	71	6	35.5		
18	-196	2	0.21	0.14	200	1	1000 NF <sub>3</sub> + 100 BF <sub>3</sub> + 66 F <sub>2</sub> (initially); 2 x 200 NF <sub>3</sub> /45 2 x 100 BF <sub>3</sub> /30 4 x 33 F <sub>2</sub> (25 intervals); 3 x 100 NF <sub>3</sub> /BF <sub>3</sub> NF <sub>3</sub> /BF <sub>3</sub> (10-15 intervals)	60-40	SB	12	H(A)	49	H(A)	24.5		
19	-196	2	0.21	0.29	400	1	1000 premixed NF <sub>3</sub> /BF <sub>3</sub> = 14/3 + 200 F <sub>2</sub> (initially); 3 x 100 NF <sub>3</sub> /BF <sub>3</sub> and 5 x 50 intervals)	120-60	SB	12	H(A)	70w (1)	V	-		
20	-196	2.5	0.21	0.21	300	1	1000 premixed NF <sub>3</sub> /BF <sub>3</sub> = 14/3 + 200 F <sub>2</sub> (initially); 100 F <sub>2</sub> (60) 100 F <sub>2</sub> (ini- tially); 3600 intervals)	200-100	SSS-3	12	H(A)	0	V	0		
82	-196	1	0.5	0.13	300	C	100 F <sub>2</sub> (ini- tially); 3600 premixed NF <sub>3</sub> / BF <sub>3</sub> = 2/1 + 200 F <sub>2</sub> (50)	-300	SF	7.5	GE	490	G	490		
21	-196	1.75	4.67	0.67	200	C	100 F <sub>2</sub> (ini- tially); 1700 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (105)	300-250	SSS-3	12	H(A)	142	M	47		
25	-196	2	4.67	0.56	200	C	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (120)	350-230	SB	12	H(A)	28	G	14		
26	-196	1	4.67	0.56	200	C	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (66)	350-220	SB	12	H(A)	18	G	18		
28	-196	1	4.67	0.56	200	C	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (66)	350-215	SB	12	H(A)	16	G	16		
29	-196	1	4.67	0.56	200	B (1)	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (66)	350-190	SB	12	H(A)	19	G	19		
27	-196	1	4.67	0.56	200	B (1)	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (60)	350-185	SB	12	H(A)	14	G	14		
30	-196	2	4.67	0.56	200	C	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (55)	350-145	S8	12	H(A)	45	G	22.5		
31	-196	2	4.67	0.56	200	C	200 F <sub>2</sub> (ini- tially); 2000 premixed NF <sub>3</sub> / BF <sub>3</sub> = 1/4.67 (15)	300-115	SB	12	H(A)	52	G	26		
32	-196	2	4.67	0.56	200	B	-	200-120	SB	12	H(A)	54	G	27		

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## APPENDIX I (CONT'D)

Expt. No.	Reaction Temp., °C	Photolysis Time, hrs.	Mole Ratio BF <sub>3</sub> : NF <sub>3</sub>	Total F <sub>2</sub> Used, cc	Reactant Addition Amounts (cc) and Addition Times (min)	Pressure Range (during photolysis), mm	Reactor Used (b)	Lamp to Condensed Reactant Distance (c), cm	UV Lamp Type (d)	NF <sub>4</sub> BF <sub>4</sub> Weight, mg	Method (e)	Average NF <sub>4</sub> BF <sub>4</sub> Formation Rate, mg/hr	
33	-196	2	4.67	0.2	65 B 65 C 300 C	70-60 30-25 375-300	SB SB SF	12 12 .5	H(A) H(A) GE	5B 48 495	G G G	29 24 495	
34	-196	2	4.67	0.2	65 B 65 C 300 C	70-60 30-25 375-300	SB SB SF	12 12 .5	H(A) H(A) GE	5B 48 495	G G G	29 24 495	
35	-196	1	1.77	0.15	300 C	undetermined	SF	7.5	GE	655	G	655	
36	-196	2	1	0.17	200 B	85-50	SB	12	H(A) 49.5%T H(A)	43	G	21.5	
37	-196	2	1	0.17	200 B	80-45	SB	12	H(A) 49.5%T H(A)	46	G	23	
38	-196	2	1	0.17	200 B	80-55	SB	12	H(A) 36.3%T H(A)	34	G	17	
39	-196	2	1	0.17	200 B	80-50	SB	12	H(A) 33.0%T H(A)	27	G	13.5	
40	-196	2	1	0.17	200 B	-	SSS-3	12	H(A) H(A)	14	W	14	
41	-196	2	1	0.17	200 B	-	SSS-3	12	H(A) H(A)	20	W	10	
42	-196	2	1	0.17	200 B	-	SSS-3	12	H(A) H(A)	59	W	29.5	
43	-196	1	1	7.8	1165 C	1165 F <sub>2</sub> (initially); 300 premixed NF <sub>3</sub> BF <sub>3</sub> = 1/1 (50)	undetermined	ST	7	H(A) H(A)	trace	trace	35
44	-196	2	1	7.8	1165 B	660 F <sub>2</sub> (initially); 300 premixed NF <sub>3</sub> BF <sub>3</sub> = 1/1 (50)	undetermined	SB	12	H(A) H(A)	70	W	31.5
45	-196	2	1	7.8	1165 C	660 F <sub>2</sub> (initially); 300 premixed NF <sub>3</sub> BF <sub>3</sub> = 1/1 (50)	undetermined	SB	12	H(A) H(A)	63	W	40
46	-196	1	1	2.3	145 B	85% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	260-240	SB	12	H(A) H(A)	80	W	40
47	-196	2	1	0.67	>800 (1) B	25% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	250-175	SB	12	H(A) H(A)	66	W	33
48	-196	2	1	0.67	800 (1) B	25% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	275-215	SB	12	H(A) H(A)	80	W	40
49	-196	2	1	0.67	800 B	25% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	220-165	SB	12	H(A) H(A)	66	W	33
50	-196	2	1	0.5	600 B	-	190-140	SB	12	H(A) H(A)	80	W	40
51	-196	2	1	0.5	600 B	-	175-125	SB	12	H(A) H(A)	82	W	41
52	-196	2	1	0.42	500 B	-	145-95	SB	12	H(A) H(A)	74	W	37
53	-196	2	1	0.33	400 B	-	125-70	SB	12	H(A) H(A)	72	W	36
54	-196	2	1	0.25	300 B	-	100-60	SB	12	H(A) H(A)	54	W	27
55	-196	2	1	0.17	200 B	-	110-70	SB	12	H(A) H(A)	65	W	32.5
56	-196	2	1	0.17	200 B	-	100-65	SB	12	H(A) H(A)	61	W	30.5
57	-196	2	1	0.17	200 B	-	130-70	SB	12	H(C) H(A)	60	W	30
58	-196	2	1	0.08	100 B	-	55-30	SB	12	H(C) H(A)	57	W	28.5
59	-196	4	1	0.30	600 B	33% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	180-90	SB	12	H(C) H(A)	58	W	29
60	-196	4.5	1	0.67	100 -	33% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	150-100	SR	12	H(A) H(A)	71	W	35.5
61	-196	3	1	0.29	200 I	100 F <sub>2</sub> + 100 premixed NF <sub>3</sub> /BF <sub>3</sub> BF <sub>3</sub> = 1/1 (2/0)	150 ± 20	SB	12	H(A) H(A)	75	W	37.5
62	-196	4	1	0.30	600 B	33% F <sub>2</sub> added before NF <sub>3</sub> + BF <sub>3</sub>	200-125	SB	12	H(A) H(A)	145	W	36.2
63	-196	4.5	1	0.67	100 -	100 F <sub>2</sub> + 100 premixed NF <sub>3</sub> /BF <sub>3</sub> BF <sub>3</sub> = 1/1 (2/0)	150 ± 20	SB	12	H(A) H(A)	38	W	38
64	-196	3	1	0.29	200 I	2 x 50 F <sub>2</sub> + 50 premixed NF <sub>3</sub> /BF <sub>3</sub> NF <sub>3</sub> /BF <sub>3</sub> = 1/1	150 ± 20	SB	12	H(A) H(A)	60	W	20

57	-196	2	1	0.08	100	B	-	55-50	SB	12	H(C)	57	28.5
44	-196	2	1	0.33	200	B	-	180-90	SB	12	H(C)	58	29
66	-196	2	1	0.30	600	B	33% F2 added before NF3	150-100	SR	12	H(A)	71	35.5
57	-196	2	1	+ BF3	33% F2 added before NF3	-	180-120	SB	12	H(A)	75	37.5	
58	-196	2	1	0.30	600	B	+ BF3	200-125	SB	12	H(A)	145	36.2
59	-196	4	1	0.30	600	B	+ BF3	undetermined	SB	12	H(A)	38	8.4
10	-196	4.5	1	0.67	100	I	+ BF3 = 1/1 100 F2 + 100 premixed NF3/ (initially); 2 x 100 premixed NF3/BF3 = 1/1 (2/0 and 240)	150 ± 20	SB	12	H(A)	60	6
11	-196	3	1	0.29	200	I	+ 50 premixed F2 (60 intervals) 50 F2 + 200 premixed NF3/ BF3 = 1/1 (initially); 36 x 15.5 premixed NF3/BF3 = 1/1 (5 intervals); 10 x 6.2 F2 (15 intervals) 25% added before NF3	75-50	SB	12	H(A)	70	G
15	-196	3	1	0.29	112	I	+ BF3 40% F2 added before NF3 + BF3	340-250	SF	9	H(B)	165	82.5
65	-196	2	1	0.67	800	B	-	220-150	SF	9	H(B)	157	6
63	-196	2	1	0.42	500	B	+ BF3	-	SF	9	H(B)	135	78.5
60	-196	2	1	0.17	200	B	+ BF3	-	SF	9	H(B)	142	67.5
61	-196	2	1	0.17	200	B	+ BF3	-	SF	9	H(A)	89	71
62	-196	2	1	0.17	200	B	+ BF3	-	SF	9	H(A)	220	44.5
67	-196	2	1	0.17	200	B	+ BF3	-	SF	7.5	H(B)	764	110
55	-196	7	1	0.5	600	B	33% F2 added before NF3 + BF3	260-190	SF	7.5	H(B)	109	109
74	-196	3	1	0.43	600	B	17% F2 added before NF3 + BF3	500-225	SF	7.5	GE	1174	6
78	-196	1	1	0.33	400	B	25% F2 added before NF3 + BF3	-240	SF	7.5	GE	614	614
70	-196	1	1	0.33	400	B	13% F2 added before NF3 + BF3	-175	SF	7.5(m)	GE	708	708
72	-196	1	1	0.33	400	B	13% F2 added before NF3 + BF3	200-175	SF	7.5	GE	804	804
71	-196	0.5	1	0.33	400	B	13% F2 added before NF3 + BF3	-225	SF	7.5	GE	444	888
73	-196	1	1	0.33	400	B	13% F2 added before NF3 + BF3	-200	SSS-3	10.5	GE	170	170
76	-196	1	1	0.23	300	B	33% F2 added before NF3 + BF3	-350	SF	7.5	GE	705	705
79	-196	1	1	0.15	200	B	50% F2 added before NF3 + BF3	-125	SF	7.5	GE	614	614

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APPENDIX I (CONT'D)

Expt. No.	Reaction Temp., °C	Photolysis Time, hrs.	Mole Ratio BF <sub>3</sub> /NF <sub>3</sub>	Total F <sub>2</sub> Used, cc	Reactant Addition Mode (a)	Reactant Addition Amounts Added (cc) and Addition Times (min)	Pressure Range (during photolysis), mm	Reactor Used (b)	Lamp to Condensed Reactant Distance (c) cm	UV Lamp Type (d)	NF <sub>4</sub> BF <sub>4</sub> Weight mg	Average NF <sub>4</sub> BF <sub>4</sub> Formation Rate, mg/hr	
69	-196	0.25	1	0.17	200	B	-200	SF	7.5	GE	251	6	
75	-196	0.25	1	0.17	200	B	-175	SF	7.5	III	293	6	
77	-196	1	0.33	400	C	NF <sub>3</sub> /BF <sub>3</sub> /F <sub>2</sub> premixed	-250	SF	7.5	GE	723	6	
B3	-196	2	1	0.12	300	C	100 F <sub>2</sub> + 50 premixed NF <sub>3</sub> /BF <sub>3</sub> = 1/1 (initially); 5000 premixed NF <sub>3</sub> /BF <sub>3</sub> /F <sub>2</sub> = 1/1/0.883 (13%) in 30; 39% in 50; 79% in 60; 100% in 120)	500-175	SF	7.5	GE	1226	6
												613	
												647	
84	-196	4	1	0.21	390	I	-200	SF (n)	7.5	GE	2558	6	

(a) <sub>B</sub> = Before photolysis  
<sub>C</sub> = Continuous during photolysis (or for time specified)  
<sub>I</sub> = Intermittant addition of specified reactants at time specified

(b) <sub>TS</sub>  
<sub>SSS-8</sub> = 2" sapphire window on 9" Teflon test tube  
<sub>SSS-3</sub> = 2" sapphire window on 8" 347 stainless steel tube  
<sub>ST</sub> = 2" sapphire window on 3" 347 stainless steel tube  
<sub>SB</sub> = 0.5" o.d. x 3" silica tube  
<sub>SF</sub> = 3" diameter flat-windowed x 1.25" silica vessel  
<sub>S</sub> = 1/2" diameter sapphire tube

(c) Or distance to reactor bottom if no condensed phase was present.

(d) <sub>H(X)</sub> = 100W Hanovia Utility Lamp (letter designation for individual bulbs)

<sub>GE</sub> = 1000W BH6 High Pressure Mercury Arc Lamp, General Electric  
<sub>III</sub> = 1000W BH6-1-B High Pressure Mercury Arc Lamp, Illumination Industries, Inc.

(e) <sub>G</sub> = Weight determined gravimetrically (but not corrected for changing tare of silica reactors)  
<sub>M</sub> = Weight calculated from pressure decrease after photolysis (manometric method)  
<sub>V</sub> = Visual estimate

(f) Pressure before photolysis.

(g) ClF<sub>5</sub> also added; Mole ratio ClF<sub>5</sub>/NF<sub>3</sub> = 0.15 (Experiment 6); ClF<sub>5</sub>/NF<sub>3</sub> = 0.1 (Experiments 7 and 8).

(h) Temperature cycled between ambient and -196 °C twelve times.

(i) Reactor leaked after photolysis and solid product was partially hydrolyzed.

(j) All reactants introduced exactly as in experiment 29 but before photolysis.

(b) All reactants introduced exactly as in Experiment 12

(b) TS-4 = 2" sapphire window on 9" Teflon test tube  
SSS-8 = 2" sapphire window on 8" 347 stainless steel tube  
SSS-3 = 2" sapphire window on 3" 347 stainless steel tube  
ST = 0.5" o.d. x 3" silica tube  
SB = 3" diameter silica bulb  
SF = 3" diameter flat-windowed x 1.25" silica vessel  
S = 1/2" diameter sapphire tube

(c) 0r distance to reactor bottom if no condensed phase was present.

(d) H(X) = 100w Hanovia Utility Lamp (letter designation for individual bulbs)

GE = 1000w BH6 High Pressure Mercury Arc Lamp, General Electric  
III = 1000w BH6-1-B High Pressure Mercury Arc Lamp, Illumination Industries, Inc.

(e) G = Weight determined gravimetrically (but not corrected for changing tare of silica reactors)  
M = Weight calculated from pressure decrease after photolysis (manometric method)  
V = Visual estimate

(f) pressure before photolysis.

(g) ClF<sub>5</sub> also added; Mole ratio ClF<sub>5</sub>/NF<sub>3</sub> = 0.15 (Experiment 6); ClF<sub>5</sub>/NF<sub>3</sub> = 2.3 (Experiment 5); ClF<sub>5</sub>/NF<sub>3</sub> = 0.1 (Experiments 7 and 8).

(h) Temperature cycled between ambient and -196 C twelve times.

(i) Reactor leaked after photolysis and solid product was partially hydrolyzed.

(j) All reactants introduced exactly as in experiment 29 but before photolysis.

(k) Premixed NF<sub>3</sub>/BF<sub>3</sub> added to reactor before F<sub>2</sub>.

(l) Some uncertainty in amount of F<sub>2</sub> but over 800 cc.

(m) Lamp inadvertently placed off center of reactor.

(n) Reactor inlet in center of photolysis zone.

APPENDIX II. LARGE SCALE UV-SYNTHESIS OF  $\text{NF}_4\text{BF}_4$  (a)

Run No.	Reactor	Pressure Range, mm Feed Line	Feed Cycle ON(sec)-OFF(min)	Lamp-Cold Face Distance, cm	Estimated Average UV Intensity w/cm <sup>2</sup> x 100	Photolysis Time, hours	$\text{NF}_4\text{BF}_4$ Average Rate, g/hour
1	615-692	-838	0.15-0.50	4.2	2.4 (85)	4	0.50
2	267+590 (b)	-950	0.15-0.50	9.2	2.5 (80)	2	0.90
3	494-538	-924	0.30-0.50	4.2	2.4 (85)	7	1.50
4	538-569	-985	0.30-0.50	6.7	2.8 (82.5)	2	0.36
5	473-590	-985	0.30-1.00	6.7	2.0 (85)	4	1.15
6	446-515	-940	0.30-1.00	4.2	2.0 (85)	3.5	0.97
7	472-583	-964	0.30-1.50	4.2	2.0 (85)	3	1.62 (c)
8	333-357	-956	0.30-0.33	4.2	1.8 (85)	1	
9(d)	590+827 (b)	-1020	0.30-0.50	4.2	2.2 (85)	7	2.36 (c)
10(d)	505-540	-1020	0.30-0.50	4.2	1.8 (85)	7	1.86 (c)
11(d)	503-554	-964	0.40-0.50	4.2	2.1 (85)	12.5	
12	495-555	-940	0.30-0.50	4.2	1.8 (85)	15	1.33 (c)
13(e)	534-600	-940	0.30-0.50	4.2	3.2 (85)	5	
14	380-430	-958	0.30-0.50	4.2	2.3 (85)		1.43
15	580-650	-920	0.30-0.50	4.2	2.0 (85)		
16(d)	600-625	-910	0.30-0.50	4.2	1.8 (85)		
17(d)	515-545	-1050	0.30-0.50	4.2	2.4 (85)		
18(d,e)	520-550	-1080	0.60-1.00	4.2	1.9 (85)		0.83 (c)
19	480-580	-1080	0.60-1.00	4.2	2.1 (85)		2.90
20(e)	506-540	-1190	0.60-1.50	4.2	2.1 (85)		1.72 (c)
21	500-540	-1130	0.60-2.00	4.2	2.3 (85)		1.67 (c)

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(a) Equimolar  $\text{NF}_3\text{-BF}_3\text{-F}_2$  used as reactant feed mixture for all runs. Product scraped from reactor cold face at 30 min. intervals (Runs 1-8) or 15 min. intervals (Runs 9-18).

(b) Pressure in reactor not relieved after each scrapping of reactor cold face.

(c) Includes normal product hold-up of reactor which had been mechanically transferred to  $\text{NF}_4\text{BF}_4$  receiver.

(d) Reactor cold face normally refrigerated with  $\text{LN}_2$  at about atmospheric pressure except for Runs 9, 10 and 11 (20 psig); Run 16 and 18 (22 psig); and Run 17 (14 psig).

(e) Reactor disassembled and washed at conclusion of run.

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